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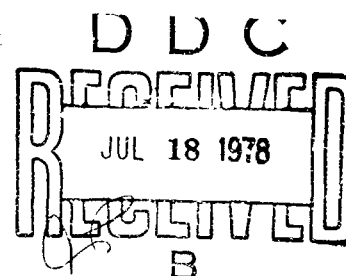
ENVIRONMENTAL QUALITY STANDARDS RESEARCH ON WASTEWATERS OF
ARMY AMMUNITION PLANTS

by

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Research Division

June 1978



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

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(U) Studies on the characterization of wastewaters from Army manufacture of trinitrotoluene (TNT), glyceryl trinitrate (trinitroglycerine, TNG), and nitrocellulose (NC) are described. The studies were undertaken to provide information to be used in design of toxicological experiments for the purpose of assigning water quality guidelines. The complexity of the chemical characterization became evident by the fact that in TNT wastewaters alone (toward which most of (Continued on reverse side)			

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20. ABSTRACT (Continued)

the effort was directed), more than 40 organic compounds were detected by GLC and TLC in addition to inorganic materials and organic aggregates not resolvable by TLC. Furthermore, the wastes from TNT loading and manufacturing plants varied among different plants, within a single plant, and in samples from a single site taken at different times. Because of the large number of components and the impracticability of toxicologically evaluating each individual compound, methodology was developed for separation of the pollutants into three major fractions, i.e., neutral organics soluble in benzene or chloroform, ionic water-soluble organics, and amorphous materials insoluble in water as well as in organic solvents. The separation of the ionic water-soluble organics, highly colored bodies, that resulted from the photodegradation of the various nitrotoluenes was achieved by means of the phase-transfer agent tetrabutyl-ammonium sulfate. It was found that wastewater samples deteriorated on storage. The problem of uniformity and storage stability for extended biological experiments at various laboratories was solved through lyophilization. It was established that lyophilized samples that were subsequently reconstituted to their original concentrations were essentially identical to the controls in composition. Photolytic studies revealed that some of the nitro bodies are more refractory toward sunlight than others and, therefore, are expected to prevail in the waters for longer periods of time.

Extraction methods were developed for separation of the organic materials contained in NG wastewaters. Results of GC and TLC showed a complex mixture of mononitrate, dinitrate and trinitrate esters of glycerol and a number of unidentified compounds, two containing the carbonyl function. Products were a function of time from sampling, of pH, and of amount of exposure to light. Lyophilization of samples containing high concentrations of salts appears to be feasible without risk of explosion.

Polarized light and electron microscopy of nitrocellulose wastewaters showed fibers from a few to several hundred nm in length and of a varying degree of nitration, together with fine particulate material, brown amorphous slime, and a crystalline precipitate. Suspended particles could be coagulated by either dialysis or addition of ionic solutes. Further characterization of nitrocellulose wastes was deemphasized after preliminary toxicological results indicated low toxicity.

PREFACE

The work described in this report was authorized under Project 1W762710AD6001, Medical Research and Development Command, Surgeon General's Office, Number 3728, Environmental Quality Standards on Wastewaters of Army Ammunition Plants. This work was conducted from 1 July 1973 through 30 June 1975. Experimental data are contained in notebooks numbers MN 2508, MN 2526, MN 2583, TSD 9003, and TSD 9113.

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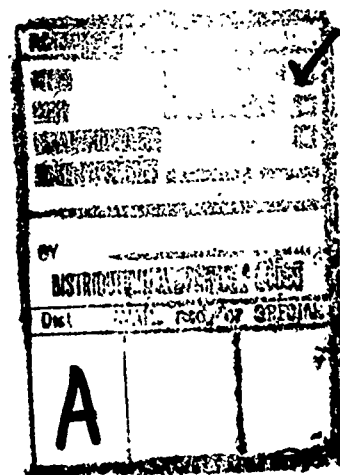
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The authors are indebted to Dr. David H. Rosenblatt of the Environmental Quality Division, Research and Development Laboratory for many helpful discussions and especially for his analysis of the problems associated with characterization of nitrocellulose wastewaters.

We are grateful to LTC Leroy H. Reuter and LTC Robert P. Carnahan of the US Army Medical Research and Development Command, and MAJ Charles A. Sorber of the Environmental Quality Division, US Army Medical Bioengineering Research and Development Laboratory for their support and guidance.

The experimental work for part I was conducted by Eleanor V. Crabtree, Joseph W. Hovanec, Leon J. Schiff, George T. Davis, Norman C. Thomas, and Aubrey E. Cooper; that for part II was conducted by Joseph Hovanec, Peter Zvirblis, Eleanor V. Crabtree, and CPT Neil L. Sass; and that for part III was conducted by CPT Gary Horton, Mary M. Demek, and William Mayer.



INTRODUCTORY NOTES

This study was supported by the Office of the Surgeon General to provide information to be used in the design of toxicity studies leading to guidelines and eventually to assignment of water quality standards for wastewaters from Army ammunition plants. The wastes of interest stem from facilities that manufacture or use trinitrotoluene (TNT), nitroglycerine (TNG), or nitrocellulose (NC). The general objectives were approved by a board from the National Research Council of the National Academy of Sciences.

The report is divided into three major parts, each treated as an entity, with the following titles:

TNT Wastewater Studies
Analysis of Nitroglycerine Wastewater, and
Characterization of Nitrocellulose Wastewater.

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ENVIRONMENTAL QUALITY STANDARDS RESEARCH ON WASTEWATERS OF
ARMY AMMUNITION PLANTS

PART I. TNT WASTEWATER STUDIES

by

Eleanor V. Crabtree
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PART I. TNT WASTEWATER STUDIES

INTRODUCTION.

Industrial facilities engaged in the production and loading of 2,4,6-trinitrotoluene (α -TNT) generate large volumes of aqueous wastes that contain organonitrogen compounds. Scrubbing operations, overflows, spills, and wash-down drain water are primary sources of the waste at manufacturing installations. Steaming of rejected shells and the wash-down of floors, equipment, and filters are responsible for the generation of loading plant wastewater.

Although steps are taken to prevent their incorporation into wastewaters,¹ some of the nitroaromatic compounds associated with the manufacture of α -TNT find their way into the wastewaters of these facilities. Upon exposure to sunlight, the wastewaters turn pink to red. The pink coloration is due mainly to the photolytic decomposition of TNT. However, a contribution to the color by photolytic decomposition of impurities in α -TNT is probable. Furthermore, it is unlikely that the same compounds will be present in two samples exposed to irradiation for different lengths of time and at different pH levels.

Many compounds found in the process waters during manufacture of TNT,²⁻⁴ in TNT samples after various stages of purification,²⁻⁵ in aqueous TNT solutions exposed to sunlight⁶ or mercury lamp irradiation,^{6,7} and in the red water condensate (the distillate from a current process for disposal of TNT manufacturing wastes)⁸ are included in table I-1. Other compounds found in process wastes are 3-hydroxy-4,6-dinitrobenzoic acid;² 2-hydroxy-3,3',5,5'-tetranitrodiphenylmethane;² 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane;⁵ 2-amino-4,6-dinitrobenzoic acid;⁷ 3,5-dinitrophenol;⁷ 2,4,6-trinitroxylylene;² dinitroxylylene;⁸ 2,4,6-trinitroethylbenzene;² α -nitro-2,4,6-trinitrotoluene;² 2,4,6-trinitro-*m*-cresol;² 2,2',6,6'-tetranitroazoxytoluene;⁶ 2,4'-dimethyl-3,3',5,5'-tetranitro-*ONN*-azoxybenzene;⁶ 4,6-dinitro[1,2] benzisoxazole;⁷ and *N*-(2-carboxy-3,5-dinitrophenyl)-2,4,6-trinitrobenzamide.⁷ In wastes emanating from loading plants one would also expect to find hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) along with their degradation products.

In this report, we present studies which have a bearing on the establishment of environmental standards for effluents from TNT plants. We seek to shed more light on the following issues: (a) which compounds are present in specific wastewaters of TNT loading or manufacturing facilities, (b) whether the compounds vary among TNT plants performing similar operations, e.g., loading or manufacturing, (c) whether the compounds found in wastes vary within a single TNT plant, (d) what effect sunlight has on the compounds found in wastewaters, (e) which components in wastes resist change during the period prior to discharge into public waters, and (f) in what ways can stable waste samples be prepared for meaningful toxicological studies over long periods. The development of considerable analytical methodology was required to characterize the wastes. The techniques used for fingerprinting (showing that the same compound exists although its absolute identity may not be known) as well as identifying some of the waste products are included.

Table I-1. Chromatographic Data and Occurrence of Reference Compounds

Compound	GC ^a retention time	LC ^b retention volume	R _F values ^c		Color reactions ^d		Occurrence
			S1	S2	EDA(R1)	Other	
	min	ml					
2-Nitrotoluene	79	2.66	59	75	None	—	A
3-Nitrotoluene	90	2.83	59	75	None	—	A
4-Nitrotoluene	88	2.70	57	75	None	—	A
1,4-Dinitrobenzene	181	2.20	53	75	None	—	B
1,3-Dinitrobenzene	191	2.46	44	75	Lavender	—	A, B, C
2,6-Dinitrotoluene	204	2.84	48	75	None	—	A, B
1,2-Dinitrobenzene	216	—	31	71	None	—	—
2,5-Dinitrotoluene	248	2.70	54	76	Yellow	—	A, B, C
2,4-Dinitrotoluene	262	2.97	45	75	Blue	—	A, B, C
2,3-Dinitrotoluene	277	3.07	37	73	Yellow	—	A, B, C
3,5-Dinitrotoluene	279	—	48	76	Lavender	—	A, C
3,4-Dinitrotoluene	327	4.03	37	75	Yellow	—	A, B
1,3,5-Trinitrobenzene	327	2.10	49	77	Red	—	A, B, C, D, E
2,4,6-Trinitrotoluene	392	3.09	53	77	Red-brown	—	A, B, C, D, E
2,3,6-Trinitrotoluene	416	3.42	45	76	Orange-red	—	A
2,3,5-Trinitrotoluene	455	3.36	42	75	Orange	—	A, B
2,4,5-Trinitrotoluene	473	3.28	43	74	Orange	—	A, B
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	473	1.88	4	f	None	—	—
2,4,6-Trinitrobenzaldehyde	483	2.36	33	77	Red	R2	A, D, E
2,3,4-Trinitrotoluene	510	3.83	22	68	Yellow	—	A, B
3,4,5-Trinitrotoluene	546	3.44	26	70	Yellow	—	A
2,4,6-Trinitrobenzyl alcohol	569	1.96	13	77	Dark red	—	A, C
2,4,6-Trinitrobenzoic acid	—	2.10	0	27	Red	R3	A, E
2,2',4,4',6,6'-Hexanitrobiphenyl	—	12.6	38	79	Purple-red	—	F
2,2',4,4',6,6'-Hexanitrodiphenylmethane	—	—	38	73	Purple	—	—
4,6-Dinitroanthranil	—	—	40	81	Rose-red	—	D, E
2,4,6-Trinitrobenzonitrile	—	—	28	80	Ochre	—	D, E
4,6-Dinitro-o-cresol	—	—	4	35	Yellow	R3	A
2-Carboxy-3,3',5,5'-tetranitroazoxybenzene or 2'-carboxy-3,3',5,5'-tetranitroazoxybenzene	—	—	0	43	Blue-purple	R3	A, E
Picric acid	—	—	0	41	Yellow	R3	A
2,6-Dinitro-p-cresol	—	—	0	23	Orange	R3	A
2,5-Dinitrobenzoic acid	—	—	—	16	Yellow	R3	—
3,5-Dinitrobenzoic acid	—	—	0	11	Lavender	R3	—
4-Nitrobenzoic acid	—	—	0	9	None	R3	—
3-Nitrobenzoic acid	—	—	0	9	None	R3	—
2,4-Dinitrobenzoic acid	—	—	0	7	Tan	R3	A
3,4-Dinitrobenzoic acid	—	—	0	5	Yellow	R3	A
2,2'-Dicarboxy-3,3',5,5'-tetranitroazoxybenzene	—	—	0	4	Blue-purple	R3	A, E
5-Nitroanthranilic acid	—	—	0	23	Yellow	R3,R4	—

^a 8% UC-W98 column. temperature program 140°C for 2 minutes, 8°C per minute to 220°C, 220°C^b C₁₈/Corasil reverse-phase column. acetonitrile-water (1:1) elution solvent.^c TLC solvents S1 = benzene-cyclohexane-ethyl acetate (50:45:5), S2 = benzene-ether-ethanol (50:30:20).^d Detection reagents R1 = ethylenediamine (EDA), R2 = 2,4-dinitrophenylhydrazine, yellow, R3 = 2,6-dichloroindophenol sodium salt, pink or rose, R4 = modified Ehrlich's reagent, purple. Each compound was tested with all four reagents; only positive responses are shown.^e A = continuous TNT process; B = military grade TNT, C = red water condensate, D = sunlight photolysis of α-TNT, E = mercury lamp irradiation of α-TNT, F = byproduct of purification step.^f Smear.

II. EXPERIMENTATION.

A. Materials and Methods.

1. Reference Compounds.

Practical grade α -TNT was recrystallized from ethanol, then recrystallized from carbon tetrachloride. The compounds 2,6-dinitrotoluene (2,6-DNT) and 2,4-dinitrotoluene (2,4-DNT) were recrystallized from methanol. The compound 1,3,5-trinitrobenzene (*s*-TNB) was prepared by decarboxylation of 2,4,6-trinitrobenzoic acid (TNBA), and was then recrystallized from glacial acetic acid and washed with ethanol and ether. The recrystallized samples were all pure by gas chromatographic (GC) and thin-layer chromatographic (TLC) analysis. (Samples for use as standard compounds were shipped to five Surgeon General's Office contractors involved in aquatic survey and toxicity studies near ammunition plants.)

White compound (2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene) was obtained as an aqueous slurry from the continuous TNT process of the Radford Army Ammunition Plant (RAAP). Washed with distilled water and air-dried, the crude material melted at 255°C to 257°C, with decomposition; recrystallized from ether, it melted at 250°C to 256°C, with decomposition (lit. 245°C,⁶ 255°C⁹). Thin-layer chromatography on Q5 silica gel plates (Quantum Industries) with the solvent benzene-ether-ethanol (50:30:20) and visualization with ethylenediamine-dimethyl sulfoxide (EDA-DMSO) (1:1) spray gave a deep purple spot near the start ($hR_f = \sim 4$); the crude sample gave, in addition, a pink spot at $hR_f = 28$ and faint spots at $hR_f = 43$ and 81 (hR_f values are not precise constants, but are used throughout this report to show the relative locations of thin-layer chromatography spots on the plates; $hR_f = R_f \times 100$).

Monocarboxy white compound (2-carboxy-3,3',5,5'-tetranitroazoxybenzene or 2'-carboxy-3,3',5,5'-tetranitroazoxybenzene) was prepared by aqueous reflux of white compound until the product gave a single spot by TLC ($hR_f = 43$, purple with EDA-DMSO), melting point 213°C to 215°C (lit.⁹ 215°C).

The Infrared (IR) and nuclear magnetic resonance (NMR) spectra were consistent with the structures of both white compound and monocarboxy white compound. For the recrystallized white compound the NMR spectrum (CD₃OD) yielded the results shown in table I-2 — two exchangeable protons and two rings with four ring proton; meta to each other. The NMR spectrum for monocarboxy white compound showed five aromatic ring protons. The mass spectra showed the existence of fragments consistent with these structures.

The isomers of TNT were supplied by Stanford Research Institute. Small amounts of 4,6-dinitroanthranil, 2,4,6-trinitrobenzonitrile, 2,4,6-trinitrobenzyl alcohol, 2,2',4,4',6,6'-hexanitrobibenzyl, and 2,2',4,4',6,6'-hexanitrodiphenylmethane were furnished by Naval Ordnance Laboratory. Other nitroaromatic compounds used as chromatographic standards were purchased from commercial sources.

Table I-2. Nuclear Magnetic Resonance Peaks for White Compound

Absorbance	Relative integral	Coupling constant	Functionality
ppm		Hz	
4.82	2	—	Carboxyl, protons
9.00	1	2	Four ring protons, in the 4,4', 6, and 6' positions
9.12	1	1	
9.13	1	1	
9.40	1	2	

2. Water Samples Studied.

The water samples were the following: (a) synthetic solutions of polynitroaromatic compounds and (b) actual wastewaters from Army ammunition plants (12 samples of wastewaters from four manufacturing or loading plants, table I-3). The α -TNT content of the wastewaters varied between <1 ppm (after a charcoal filter) and about 100 ppm (catch basin before filters). Solutions of about 100 ppm of α -TNT were prepared by passing distilled water or aqueous buffer slowly (less than 0.5 l/min) through a column of recrystallized α -TNT.

3. Sample Preparation.

Preliminary fractionations of the organic components in wastewaters and in irradiated TNT solutions were accomplished using either of two extraction schemes. In one scheme, the wastewater was extracted with chloroform to obtain the neutral fraction. Then, tetrabutylammonium sulfate (TBAS) was added in aqueous solution (pH = 7) to the water layer and anions of acidic materials such as carboxylic acids and phenols were extracted into chloroform as ion pairs with tetrabutylammonium cation.

When the alternative separation scheme was used, the wastewater was extracted with benzene to obtain the neutral fraction. The water layer was next extracted with ether. The aqueous phase was filtered to remove insolubles, then adjusted to pH = 1 with concentrated hydrochloric acid, and again extracted with ether.

To prepare the extracts for chromatographic analysis, aliquots were evaporated to dryness and redissolved in small volumes of organic solvent. Addition of a few milliliters of propylene glycol prior to evaporation prevented the tendency of the material to adhere to the walls of the flask and to resist attempts to redissolve it.

Table I-3. TNT Wastewater Samples

Designation	Sampling site	Color	pH*	pH**
RAAP-CT-7/73	Final wash catch tank, composite (10 samples)	Yellow	2.25	—
RAAP-ST-1/74	Composite (3 samples) after settling and sludge tanks	Yellow to rust	7.5–8.0	8.25
RAAP-CT-1/74	Final wash catch tank	Brick red	4.5	2.85
HAAP-S-9/73	Effluent scrubber, Incorporation Building (J-8)	—	6.2	7.9
HAAP-D-9/73	Decant from Composition B, Incorporation Building (J-8)	—	6	3.8
HAAP-HT-9/73	Holding tank, Dewatering Building (H-4)	—	2.4	—
LAAP-S-8/73	Sump area, pit S	—	—	—
LAAP-BG-1/8/73	Sump area, pit BG-1	—	—	7.8
JAAP-CB-8/73	Catch basin, before filters	Reddish yellow	5.5	—
JAAP-CF-8/73	After charcoal filter	Colorless	6.0	—
JAAP-PF-8/73	Effluent from diatomaceous earth filter	Reddish yellow	7.0	—
JAAP-PF-12/74	Effluent from diatomaceous earth filter	Light orange	6.8	—

* Onsite test with pH indicator paper.

** Measured on Beckman model G pH meter.

4. Chromatographic Methods.

A Hewlett-Packard model 7610 gas chromatograph equipped with a temperature programmer and flame ionization detector was used. Two 2-mm ID glass columns, 4 feet in length, were used: one with 3.8% UC-W98 with a program of 160°C and 2 minutes, 8°C per minute to 200°C for 10 minutes, and the other with 8% UC-W98 with a program of 140°C for 2 minutes, 8°C per minute to 220°C for 4 minutes. All GC data were processed by an Autolab System IV computing electronic integrator (Spectra-Physics), which yields retention times and relative peak areas.

The high-pressure liquid chromatography (HPLC) data were obtained by a DuPont model 830 liquid chromatograph with a 254-nm fixed-wavelength ultraviolet detector. Two columns were used: 1 2.1-mm by 50- or 100-cm stainless steel column of C₁₈/Corasil reverse-phase packing (Waters Associates), and a normal-phase Corasil II packing.

For TLC, commercially prepared silica gel layers on glass plates, types Q5, Q5F, LQD, and LQDF (Quantum Industries), were used with a Gelman TLC chamber. Relatively nonpolar materials were developed with benzene-cyclohexane-ethyl acetate (50:45:5); the more polar materials were developed with either benzene-ethanol (50:30:20) or chloroform-ethanol (90:10). (TNT and other neutral fraction materials, as well as the ether-extracted compounds, chromatographed as round spots of constant R_f values with increasing load. In contrast, the ion-paired materials migrated as crescent-shaped spots with R_f values dependent on the amount of substance applied to the plate. Since the actual concentrations of the components in the wastewaters were not known, R_f values of the ion-paired materials were considered as merely guide values. The deep, characteristic colors of the TBAS-complexed color bodies, however, aided fingerprinting, and a distinctive TLC pattern was obtained for each wastewater sample.) The colors of the spots were noted and the chromatograms were viewed during exposure to ultraviolet (254- and 366-nm) light. The chromatograms were then sprayed with ethylenediamine-dimethyl sulfoxide (1:1) (EDA-DMSO) or other detection spray. A Kodak Ektographic Visualmaker was used for permanent photographic records of TLC chromatograms, and as a supplement to tabulation of hR_f values, spot colorations, and intensities.

Selective colorimetric detection tests were used to distinguish compounds in TNT wastewaters with similar hR_f values and color reaction with EDA spray reagents, or to give supporting identification of spots of unknown materials on TLC plates. Several spray reagents, listed in table I-4, were tested with reference compounds applied as spots to silica gel TLC plates, and with chromatograms of extracts of TNT wastewaters and photolyzed TNT solutions. Interpretation of the specific colorimetric tests required prior observation of natural colors and general effects of acids or bases used in conjunction with the spray reagents; the appropriate control tests were included in evaluating each reagent.

5. Photolysis Apparatus.

A jacketed photochemical reaction vessel (Ace Glass Co., Part Nos. 6523, 6516, and 6515) with a Hanovia 400-watt, high-pressure mercury vapor lamp in a quartz cold finger was used for irradiation of aqueous solutions. Except as otherwise indicated, the apparatus was fitted with a Pyrex filter.

Table I-4. Functional Group Spray Reagents for Thin-Layer Chromatograms

Reagent	Preparation and use	Type of compounds	Colors	Reference
Ethylenediamine	Equal amounts of ethylenediamine and dimethyl sulfoxide Undiluted	Aromatic nitro Dinitrotoluenes	Various Various	4 4
3,3'-Iminobispropylamine (3,3'-diaminodiisopropylamine)	30%, in pyridine	Nitro	Various	22
Tetraethylenepentamine	30%, in pyridine	Nitro	Various	23
2,4-Dinitrophenylhydrazine	0.4% in 2N HCl	Aldehydes and ketones	Yellow to red	24
Basic fuchsin	Spray reagent*	Aldehydes	—	24
Bromocresol green	0.3 gm bromocresol green in 20 ml water plus 80 ml methanol and 8 drops 30% NaOH, "bromocresol green spray reagent according to Stahl".	Carboxylic acids	Yellow spots on green background	24 13
2,6-Dichloroindophenol,	0.1% in ethanol. Heat briefly after spray	Organic acids	Red spots on blue background	13
<i>p</i> -Dimethylaminobenzaldehyde	Modified Ehrlich's spray reagent*	Aromatic amines	Various	13
4-Chloro-7-nitrobenzo-2,1,3-oxadiazole (NBD chloride)	Spray with freshly prepared 1% methanolic NBD chloride. After 3 to 5 minutes, spray with saturated solution of sodium acetate in ethanol. Heating at 110°C intensifies colors.	Amino compounds	Various	10-12
Ferric chloride	2% in water or in methanol	Phenols	Blue	13, 14
Ferric chloride - Potassium ferricyanide	Mix equal amounts of 1% potassium ferricyanide and 2% ferric chloride just before use. Colors are intensified by subsequent spraying with 2N HCl.	Aromatic amines, phenols, compounds with reducing properties	Blue	13, 14
4-Nitrophenyldiazonium fluoborate	Spray first with freshly prepared 1% 4-nitrophenyldiazonium fluoborate in acetone, then with 0.1N methanolic KOH.	Phenols and amines capable of coupling	—	13
2,6-Dichloroquinone-chlorimide	0.1% to 1% in absolute ethanol or 0.1% to 0.2% in ethanol or in acetone. After spraying, expose to NH ₃ fumes. (Gibbs reagent).	—	—	13, 14

* Purchases from Applied Science Laboratories, Inc.

B. Results.

1. Chromatographic Data on Reference Compounds.

Table I-1 gives the basic information of GC retention times, LC retention volumes, and TLC R_f values for a number of compounds of interest. Because the GC data given in table I-1 were obtained with an 8% UC-W98 column and a specific temperature program, they cannot be used to identify wastewater components using data obtained with a different column or different temperature program.

Included in table I-1 are the responses of the compounds to selected spray reagents. In general, colors for the same compounds tested with iminobispropylamine and with tetraethylenepentamine were very similar to those with EDA. However, spot colors were more intense with iminobispropylamine and, of even more significance, were much more stable than those given with EDA. Most of the colors given with the EDA-DMSO reagent were consistent with the colors reported by Chandler *et al.*³ The dinitrotoluenes, however, gave no detectable colors with EDA-DMSO, but did react with neat EDA.

The 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent provided a sensitive and specific test for carbonyl compounds. Spots of 2,4,6-trinitrobenzaldehyde turned bright yellow on a near-white background when sprayed with 2,4-DNPH.

Both bromocresol green and 2,6-dichloroindophenol (2,6-DCIP) function as acid-base indicators. The rose-pink colored spots of 2,6-DCIP were more distinctive than the yellow spots of bromocresol green for visualization of the acidic nitro compounds.

When a modified Ehrlich's reagent was tested with 16 variously substituted aromatic amines, in addition to the reference compounds listed in table I-1, each of the amines gave a sensitive reaction, with varying colors (red, purple, dark blue). Among all the compounds in the table, only 5-nitroanthranilic acid (the sole amino compound) gave a positive reaction, turning dark blue-purple. This reagent appears to be quite sensitive and specific for aromatic amines. Although the ferric chloride reagents gave positive tests with the aromatic phenols and amines, the tests were not sensitive nor were the colors distinctive. The two dinitrocresols did not react. The ferric chloride-potassium ferricyanide reagent was generally more sensitive than ferric chloride alone.

The compound 4-chloro-7-nitrobenzo-2,1,3-oxadiazole (NBD chloride) has been used for sensitive fluorometric detection and assay of amino compounds,^{10,11} and as a colorimetric spray reagent for sulfonamides,¹² however, NBD chloride was less sensitive than the modified Ehrlich's reagent when tested with the same compounds. The compound 5-nitroanthranilic acid, which was the available compound nearest in structure to 2-amino-4,6-dinitrobenzoic acid (reported⁷ as a TNT photolysis product), did not give a useful test with NBD reagent (pink color developed after about 1 hour).

When 4-nitrophenyldiazonium fluoroborate¹³ and 2,6-dichloroquinonechloroimide^{13,14} were tested with a variety of substituted aromatic amines and phenols, the nitro-substituted compounds did not react. As explained by Feigl,¹⁵ the condensation requires that the phenol have a free *para* position and that the benzene ring not have CHO, NO₂, COO, or SO₃H groups in the position *ortho* to the phenolic OH group.

2. Product Analysis of a Photolyzed α -TNT Solution.

Preparatory to identification of wastewater components by comparison of chromatographic data, a laboratory-irradiated aqueous TNT solution (500 ppm, 6 hours' irradiation, Pyrex filter) was analyzed by TLC. The irradiated solution was extracted with benzene, then adjusted to pH = 1 and extracted with diethyl ether.

The benzene-extracted photolysis products were assigned structures (table I-5) on the basis of (a) hR_f values using benzene-cyclohexane-ethyl acetate (50:45:5), (b) EDA color reactions, and (c) previously identified⁷ TNT photolysis products. Spots after TLC with benzene-ether-ethanol (50:30:20) of the ether-extracted fraction (table I-6) are probably monocarboxy white compound at $hR_f = 43$; 2,4,6-trinitrobenzoic acid, 3,5-dinitrophenol, or both, at $hR_f = 28$; and white compound at $hR_f = 5$. Spots at $hR_f = 24$ gave a positive test with modified Ehrlich's reagent and may be 2-amino-4,6-dinitrobenzoic acid.⁷ Authentic samples of other previously reported compounds were not available.

3. Uniformity of Components in Plant Wastes.

In tables I-7 through I-14, attempts were made to match chromatographic data from various wastewater samples on the basis of retention times or hR_f values and color reactions with EDA. Tentative identification of some components of the wastes was made by comparing chromatographic data for wastewater samples with those for the reference compounds in table I-1 and for laboratory-irradiated α -TNT (tables I-5 and I-6). Several factors contribute to uncertainty in identification of materials: nonreproducibility of retention times and hR_f values, concentration dependence in TLC of ion pairs, color instability, and the large number of possible compounds. Materials with similar values are not unequivocally the same compound. For identification purposes, standards and test samples should be chromatographed using exactly the same experimental conditions.

a. Samples from the Same Plant.

Wastewaters from two sources within the Holston Army Ammunition Plant (HAAP) were analyzed. One source (HAAP-S) was the effluent of the scrubber system in the building where molten α -TNT is blended with RDX and wax to form Composition B (60% RDX, 39% TNT, and 1% wax). The other sample (HAAP-D) was taken directly from a batch of Composition B during the decant phase of processing. Four compounds were found by GC and three by TLC to be common among the neutral compounds, and three among the acidic compounds were present in both samples. However, there were six neutral compounds found in HAAP-D that were not in the sample of HAAP-S, and three compounds in HAAP-S that were not found in HAAP-D (by GC). Similarly, among the acidic compounds, the HAAP-D sample had five compounds not present in the HAAP-S sample; HAAP-S sample had two compounds not present in the HAAP-D sample (by TLC).

Table I-5. TLC Analysis of Photolyzed α -TNT. Benzene Extract

hR_f	Color with EDA-DMSO	Intensity	Tentative identification
53-55	Yellow-brown	Very strong	2,4,6-Trinitrotoluene
48	Pink	Medium	1,3,5-Trinitrobenzene
43	Yellow-orange	Weak	4,6-Dinitro[1,2] benzisoxazole ^a
38	Pink	Weak	4,6-Dinitroanthranil
34 ^b	Red	Medium-strong	2,4,6-Trinitrobenzaldehyde
18	Pink-tan	Weak	Unknown I
14 ^c	Purple-brown	Weak-medium	3,5-Dinitrophenol ^a
9	Pink-brown	Weak	2,4,6-Trinitrobenzyl alcohol
5	Purple-tan	Weak-medium	Unknown II
0	Brown	Strong	Origin material

^a No reference sample was available; identification was by analogy with data obtained by Kaplan *et al.*

^b Bright yellow with 2,4-DNPH.

^c Blue with FeCl_3 - $\text{K}_3\text{Fe}(\text{CN})_6$.

Table I-6. TLC Analysis of Photolyzed α -TNT, Ether Extract

hR_f	Color with EDA-DMSO	Intensity
75-78 ^a	Red-brown	Medium
72	Orange	Weak
59	Pink	Weak
54	Blue	Very weak
50	Lavender	Weak
45	Pink	Weak
43	Pink-purple	Weak
37	Tan	Weak
32	Rose	Medium
28 ^b	Purple-brown	Weak
24 ^c	Yellow-tan	Weak
20	Orange-tan	Medium
14	Purple-tan	Strong
12	Yellow-tan	Strong
5	Blue-purple	Strong
3	Red-brown	Medium strong
0	Dark brown	Strong

^a Mixture of relatively nonpolar compounds, resolvable with benzene-cyclohexane-ethyl acetate (50:45:5).

^b Blue with FeCl_3 - $\text{K}_3\text{Fe}(\text{CN})_6$.

^c Purple with modified Ehrlich's reagent.

Table I-7. GC Data* on Chloroform Extracts of TNT Wastewaters from Various Sources

Possible identification	RAAP-ST-1/74		HAAP-S-9/73		HAAP-D-9/73		LAAP-BG-1-8/73		LAAP-S-8/73		JAAP-PF-8/73		JAAP-CB-8/73	
	RT	Area	RT	Area	RT	Area	RT	Area	RT	Area	RT	Area	RT	Area
	sec	%	sec	%	sec	%	sec	%	sec	%	sec	%	sec	%
Undetermined	—	—	—	—	—	—	—	—	64	.5	—	—	—	—
Undetermined	—	—	—	—	—	—	—	—	71	1.3	—	—	—	—
2,6-DNT	90	1.7	—	—	98	.2	—	—	98	1.1	—	—	100	<.1
Undetermined	—	—	—	—	115	.1	—	—	—	—	—	—	—	—
2,4-DNT	121	9.5	133	.2	133	3.6	—	—	135	4.1	—	—	136	.5
Undetermined	149	.2	—	—	—	—	141	1.2	—	—	—	—	—	—
s-TNB	188	.6	197	5.3	199	.6	200	5.5	199	14.2	204	9.3	208	<.1
α-TNT	207	86.8	217	78.2	226	89.4	217	2.7	221	49.2	230	88.6	235	99.1
Undetermined	259	.2	—	—	256	1.2	—	—	258	2.3	—	—	—	—
Undetermined	283	.1	291	1.8	289	1.7	289	18.0	315	.2	294	.3	305	<.1
Undetermined	395	.1	359	6.5	344	2.8	369	42.1	329	.4	—	—	337	<.1
Undetermined	406	.1	395	6.6	437	.1	392	29.0	359	9.2	—	—	339	<.1
Undetermined	502	.6	505	1.2	504	.1	505	1.5	506	.4	—	—	401	<.1

* Variations in retention time (RT) for the same compound resulted from slight differences in instrumental conditions

Table 1-8. Spot Colors with LIDA-DMSO Spray in the TLC Analysis of TNT Containing Wastewaters.
TLC Solvent Benzene-Cyclohexane-Ethyl Acetate (50:45:5)

R_f	RAAP-ST-1/74	RAAP-CT-1/74	HAAP-S-9/73	HAAP-D-9/73	LAAP-BGJ-8/73	JAAP-CB-8/73	JAAP-PF-8/73	JAAP-PF-12/74
60	—	—	(Strong) orange-brown	(Strong) orange-brown	(Weak) orange-brown	Red-brown	Red-brown	Fluorescent
58	(Strong) orange-brown	(Strong) orange-brown	—	—	—	—	—	—
54	Pink-tan	—	Pink-tan	—	(Weak) pink-tan	Pink	Pink	Purple-brown
53	—	—	—	—	—	—	—	—
50	—	Orange-tan	—	—	—	—	—	—
48	—	—	—	Tan	—	—	—	Rose-red
44	(Bright) yellow	(Bright) yellow	—	—	—	—	—	—
36	—	Pink-orange	—	—	—	—	—	—
34	—	—	—	—	—	—	—	Trace
30	—	(Light) yellow	—	—	—	—	—	—
21	—	—	—	—	—	Yellow	Yellow	—
20	—	—	—	—	(Light) yellow	—	—	—
19	—	—	—	—	—	Pink	Pink	—
18	—	—	—	—	—	—	—	Yellow
14	—	—	—	(Weak) yellow-orange	—	—	—	Tan-purple
13	—	—	—	(Weak) yellow-orange	—	—	—	—
12	(Light) orange	—	—	—	—	—	—	—
11	—	—	—	—	—	—	—	Red-purple
10	—	—	—	(Weak) yellow-orange	—	—	—	—
9	—	—	—	—	Orange-tan	—	—	—
5	—	—	—	Orange-tan	—	—	—	Yellow-tan
4	—	Colorless (UV)	—	—	—	—	—	—
3	—	—	—	—	—	—	—	(Light) brown
0	Tan	Tan	Tan	Tan	Tan	Tan	Tan-brown	(Light) brown

Table I-9. Spot Colors in the TLC Analysis for 1BAS- Chloroform Extracts of Wastewaters,
TLC Solvent: Benzene-Ether-Ethanol (50:30:20)

<i>hR_f</i>	RAAP-ST-1/74	RAAP-CT-1/74	HAAP-S-9/73	HAAP-D-9/73	LAAP-BG1-8/73	JAAP-CB-8/73	JAAP-PF-8/73
65	-	-	-	(Light) pink	Red	-	Red-tan
64	-	-	-	-	Red-tan	-	-
61	-	-	-	-	Yellow	-	-
60	Orange	-	-	-	-	Yellow	-
58	(Light) orange	-	-	-	-	-	-
57	-	-	-	-	-	Orange	-
55	-	-	Colorless	Colorless	Orange	-	-
52	Orange	-	-	-	-	-	-
50	Yellow	-	-	-	-	-	-
46	-	Orange	-	-	-	-	-
44	Red-violet	-	-	-	-	-	-
43	-	Yellow	-	Orange	-	-	Orange-tan
41	-	-	-	Yellow	-	-	-
39	-	-	-	-	-	Orange	-
37	-	-	Yellow	-	-	-	-
36	-	Red-violet	-	-	-	-	-
33	-	-	-	(Strong) yellow	-	-	-
32	-	-	-	-	Orange-tan	-	-
30	Yellow	-	Red	-	-	-	-
29	-	Yellow	Yellow	-	-	-	-
27	-	-	-	Orange	-	-	-
25	-	-	Yellow	Orange	-	-	-
20	Orange	-	-	Yellow	-	-	-
15	-	Red	-	-	-	-	-
14	-	-	Red	-	-	-	-
13	-	Orange	-	-	-	-	-
10	Red	-	Brown	-	-	-	-
8	-	Yellow	-	-	-	-	-
5	-	-	-	Tan	-	-	-

Table I-10 Spot Colors in the TLC Analyses for TBAS-Chloroform Extracts of Wastewaters,
TLC Solvent Chloroform-Ethanol (90:10)

<i>hR_f</i>	RAAP-ST-1/74	RAAP-CT-1/74	HAAP-S-9/73	HAAP-D-9/73	LAAP-BG1-8/73	JAAP-CB-8/73	JAAP-PF-8/73
68	Tan	-	-	(Light) pink	-	-	Orange-brown
67	-	-	-	-	-	-	-
63	-	Red-tan	-	-	-	-	-
61	Yellow-orange	Yellow	-	-	-	-	-
56	(Strong) yellow	-	-	-	Red-brown	-	-
55	-	-	-	-	Orange	(Light) yellow	-
53	Red-orange-brown	Orange	-	-	Red-brown	-	-
52	-	-	-	-	Yellow	-	-
50	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-
45	-	-	-	-	-	-	-
44	-	-	Tan	-	-	Red	-
42	-	-	-	-	-	Red	-
40	-	-	-	Orange-tan	-	-	-
39	-	-	-	Yellow	-	Orange-brown	Orange-brown
38	-	Orange	Tan-orange	-	-	-	-
34	Yellow	-	-	-	-	-	-
33	-	-	-	Red-orange	-	-	-
32	-	Red-violet	-	-	-	-	-
30	-	Yellow	-	-	-	-	-
29	Orange	-	-	Red-orange	-	-	-
28	-	Orange	-	-	-	-	-
26	-	-	-	-	Yellow	-	-
25	-	-	-	Yellow	-	-	-
24	-	-	Red	-	Orange-brown	-	-
22	-	-	-	-	-	Tan	-
21	-	-	Orange-tan (fluorescent)	-	-	-	-
19	-	-	-	-	-	-	-
18	-	Red (fluorescent)	-	-	-	-	-
17	-	-	-	-	Colorless (UV)	-	-
12	-	Orange-tan	-	Red-brown	-	-	-
11	-	-	-	-	Orange-brown	-	-
7	-	-	-	-	Yellow	-	-
6	Yellow	Yellow	-	-	-	-	-
4	-	Colorless	-	-	-	-	-
3	-	-	-	-	Brown	-	-
2	-	-	Colorless (fluorescent)	-	-	-	-

Table I-11. Spot Colors^a in the TLC Analyses for Ether Extracts of Wastewaters,
TLC Solvent: Benzene-Ether-Ethanol (50:30:20)

hR_f	RAAP-ST-1/74	JAAP-PF-8/73	JAAP-PF-12/74	UV absorption
77	—	Red-brown ^b	—	Very strong
75	Red-brown ^b	—	—	—
71	Orange-tan ^c	—	—	—
69	—	Orange-tan ^c	—	Very strong
68 ^d	—	—	Red-brown ^b	—
65 ^e	—	—	Orange-tan ^c	—
62	Pink-purple	—	—	Weak
61	—	Pink-purple	—	Moderate
60	—	Pink (fluorescent)	Pink-purple	Weak
51	—	Light	—	Weak
50	—	—	Light	Weak
43	Yellow	—	—	—
43	—	Rose	—	Strong
40 ^f	—	—	Yellow-tan (o)	Weak
39	Pink-purple	—	—	—
38	—	Yellow-tan (o)	—	—
34 ^g	—	—	Pink (light)	Moderate
34	Yellow-tan (o)	—	—	—
33	—	Pink (light)	—	—
32	—	—	Purple-brown	Weak
30	—	Purple-brown	—	—
26	Purple-brown	—	—	—
25	—	Tan ^h	—	Moderate
25	—	—	Tan ^h	Weak
24	Tan ^h	—	—	—
21	Orange-tan ⁱ	—	—	—
19	—	—	Orange-tan ⁱ	—
17	Purple-brown	—	—	—
14	—	—	Purple-brown	Weak
13	Yellow (fluorescent)	—	—	—
11	—	Purple-brown	—	Strong
9	Yellow-tan	—	—	—
8	—	—	Yellow-tan	—
6	Blue-purple	—	—	—
6	—	Red-brown	—	Weak
3	Yellow-tan	—	—	—
2	—	—	Yellow-tan	—
0	(Dark) brown ^j	(Dark) brown ^j	(Dark) brown ^j	—

^a Color reactions given in table body correspond to use of detection reagent EDA.

^b Color with $\text{FeCl}_3\text{--K}_3\text{Fe(CN)}_6$ as detection reagent is dark blue.

^c Color with 2,6-dichloroindophenol as detection reagent is pink, with modified Ehrlich's reagent, blue-pink, and with $\text{FeCl}_3\text{--K}_3\text{Fe(CN)}_6$, blue-green.

^d The color given extends over the range of hR_f values 68 to 77.

^e The color given extends over the range of hR_f values 65 to 70.

^f The color given extends over the range of hR_f values 40 to 43.

^g The color given extends over the range of hR_f values 34 to 38.

^h Color with modified Ehrlich's reagent as detection reagent is purple; and with $\text{FeCl}_3\text{--K}_3\text{Fe(CN)}_6$, blue-green.

ⁱ Color with $\text{FeCl}_3\text{--K}_3\text{Fe(CN)}_6$ as detection reagent is blue-green.

^j Color with 2,6-dichloroindophenol as detection reagent is bright pink, and with $\text{FeCl}_3\text{--K}_3\text{Fe(CN)}_6$, blue-green.

Table I-12. Spot Colors with EDA-DMSO Spray* in the TLC Analyses
for Chloroform Extracts of JAAP-PF-8/73 Wastewaters After Storage,
TLC Solvent: Benzene-Cyclohexane-Ethyl Acetate (50:45:5)

hR_f	Tested 9/73	Tested 5/74	Tested 5/75
60	Red-brown	—	—
55	—	(Strong) red-brown	—
54	Pink	—	Brown
51	—	(Strong) red	—
48	—	—	Red
41	—	—	Pink
39	—	(Weak) pink	—
35	—	—	Pink
29	—	—	Yellow-orange
24	—	—	Light-purple
21	Yellow	—	—
19	Pink	—	—
17	—	—	Purple-tan
15	—	Yellow	—
13	—	Pink-tan	Purple-brown
9	—	—	Orange-brown
7	—	Yellow	Yellow-tan
4	—	—	Purple-tan
0	Tan-brown	(Moderate) brown	Tan

* Spray reagent: ethylenediamine-dimethylsulfoxide (1:1).

Table I-13. Spot Colors in the TLC Analyses for TBAS-Chloroform
Extracts of JAAP-PF-8/73 Wastewaters After Storage,
TLC Solvent: Benzene-Ether-Ethanol (50:30:20)

hR_f	Tested 9/73	Tested 5/74	Tested 5/75
64	Red-tan	—	—
60	—	Brown	—
59	—	—	Purple
58	—	(Strong) yellow	—
55	—	Red-brown	—
49	—	(Strong) yellow	—
48	—	(Narrow) orange-brown	Yellow
45	—	—	(Light) yellow
43	Orange-tan	(Narrow) orange-brown	Purple
40	—	(Narrow) brown	—
39	—	—	(Dark) yellow
35	—	—	(Bright) tan
31	—	—	(Narrow) orange-brown
15	—	(Narrow) brown	—
10	—	—	Yellow-tan
5	—	—	Pink-brown
4*	—	(Fluorescent)	—
2	—	—	Brown
0	—	—	Brown

* The observed fluorescence extended over the range of hR_f values 4 to 15.

Table I-14. Conditions for Photolysis of Aqueous α -TNT and RAAP Wastewater

Sample	Irradiation source	pH	Buffer	Irradiation time	[α -TNT]	
					Initial	Final
α -TNT	Hanovia lamp	6.0 ^a	Unbuffered	16 min	124	.6
α -TNT	Hanovia lamp	5.0	Acetate ^b	16 min	119	4
α -TNT	Hanovia lamp	7.0	Phosphate ^c	16 min	98	.5
α -TNT	Hanovia lamp	7.0	Phosphate	10 min	98	.5
α -TNT	Hanovia lamp	9.0	Borate ^c	8 min	108	1.5
α -TNT	Sunlight	5.7 ^d	Unbuffered	26 days	125	.2
α -TNT	Sunlight	5.0	Acetate	24 days	119	14
α -TNT	Sunlight	7.0	Phosphate	24 days	98	.4
α -TNT	Sunlight	9.0	Borate	7 days	112	33
RAAP	Hanovia lamp	5.0	Boric acid	9 min	24	21
RAAP	Hanovia lamp	7.0	Phosphate	16 min	22	12
RAAP	Hanovia lamp	9.0	Borate	10 min	22	.3

^a Final pH = 3.

^b 0.5 M.

^c 0.1 M.

^d Final pH = 3.6.

Two wastewaters from the Joliet Army Ammunition Plant (JAAP) post filter and catch basin gave similar results. The JAAP catch basin contains all flows of the load, assemble, and pack plant (LAP) that are to be treated for explosives removal. Water from the catch basin (CB) is passed through a diatomaceous earth filter to remove gross and suspended solids; the post filter (PF) sample is the effluent from that filter. Catch basin and post filter samples, JAAP-CB-8/73 and JAAP-PF-8/73, respectively, were collected on the same day; a second post filter sample, JAAP-PF-12/74, was collected after a 16-month interval.

Both TLC and GC of the neutral extracts showed the presence of four of the same compounds in the two JAAP-8/73 samples. However, GC also showed the existence in the CB sample of four compounds not present in the PF sample and two compounds in the PF sample not present in the CB sample. Similarly, TLC of the acidic materials showed the existence of three compounds in the PF sample not present in the CB sample.

A difference was found between the two PF wastewaters sampled 16 months apart, although many of the same compounds were present in both samples. Significantly, an intense rose-colored spot ($hR_f = 43$) in the ether extract of JAAP-PF-8/73 was missing in the JAAP-PF-12/74 sample, but was found in the latter sample after exposure to sunlight.

b. Samples from Different Plants.

TLC analyses of chloroform and ion-pair extracts from RAAP and Louisiana Army Ammunition Plants (LAAP) showed the existence of materials not present in any of the others. A compound found in wastewaters from RAAP but not in the wastewaters of JAAP or HAAP was identified as 2,4,6-trinitrobenzaldehyde. Among the ion pairs there was a red-violet spot at $hR_f = 36$ found in RAAP wastes that was unique in all the samples tested. GC analysis of the chloroform extracts showed material with retention times 141 and 149 seconds found only in wastes from RAAP and LAAP, and materials at 64 and 71 seconds that were unique to LAAP pit S.

It is not surprising that differences existed; wastes from facilities engaged in both manufacturing and loading contain not only the products of the commercial and essentially pure α -TNT but also other nitro bodies associated with production of α -TNT purified by water washing. These impurities, which are most probably the isomers of dinitrotoluene and trinitrotoluene, may, like α -TNT, undergo photolytic decomposition. If manufacturing facility wastes contain TNT isomers, one would expect to find that fingerprint analysis would show these and their decomposition products; such products would be absent from LAP wastewaters. Even if they initially contained the same chemical components, one would also expect to find differences in the fractions when the wastes are subjected to light irradiation because the rate of change into other compounds is dependent upon such factors as intensity of light, pH, and quantity and nature of dissolved solids in the water.

In fact, there were differences noted by TLC analysis of wastewater samples that had been allowed to sit in the laboratory for several months and retested. The differences, which appeared in both the neutral and ionic fractions, were due to the formation of new compounds (illustrated by tables I-12 and I-13). Although unequivocal identification of the components in the

wastewaters by comparing chromatographic data and color reactions with those for reference compounds is difficult, it was possible to identify the following compounds in the wastewaters: α -TNT, 1,3,5-trinitrobenzene, 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and 2,4,6-trinitrobenzaldehyde. By far the largest component in all the samples was α -TNT; 1,3,5-trinitrobenzene was found in relatively high amounts in the HAAP-S-9/73, JAAP-PF-8/73, and in both LAAP samples; whereas 2,4-DNT was found in relatively large amounts in RAAP-ST-1/74, HAAP-D-9/73, and LAAP-S-8/73. The compound 2,6-DNT was found in significant but smaller quantities than the other listed compounds in the latter three samples.

4. Photolysis Experiments.

a. Comparative Photolysis of Aqueous α -TNT under Natural and Artificial Conditions.

To better understand the effect of sunlight on the composition of wastestreams, studies were made on the extent of α -TNT decomposition in aqueous media under both natural and artificial irradiation after buffering to three pH levels. The conditions of the experiments are summarized in table I-14. For natural irradiation, samples of 2.5 liters were placed in Pyrex glass beakers, covered with transparent plastic film, and placed on the roof of the laboratory. For artificial irradiation, the solutions in a jacketed photochemical reaction vessel were irradiated with the unfiltered light of a Hanovia 400-watt Hg lamp.

In one set of experiments, α -TNT initially at a concentration of approximately 100 ppm in waters buffered at pH = 5 with acetate buffer, buffered at pH = 7 with phosphate buffer, and unbuffered, was subjected to the ultraviolet radiation of a Hanovia lamp. Photolysis of the α -TNT was followed by periodically analyzing chloroform extracts of the reaction mixture by GC. In a second series, run under slightly different conditions, similar studies were made on solutions buffered at pH = 7 (phosphate) and at pH = 9 (borate).

Plots of $\ln [\alpha\text{-TNT}]$ remaining with time for sets 1 and 2 are shown in figures I-1 and I-2, respectively. Because of the different conditions, comparisons are made separately for each set.

It is apparent that the rate of α -TNT decomposition is pH dependent, a higher loss of α -TNT being observed per unit of time at higher pH levels. The reaction at pH = 9 appears to follow first-order kinetics with respect to α -TNT, but at the lower pH levels the kinetics only become first order after what appears to be an induction period, with the time to induction being less as the pH is increased. There is an indication that following the induction period, the rate of TNT destruction does not depend on pH. (See k_{obs} for pH = uncontrolled and pH = 7, figure I-1; and pH = 7 and pH = 9, figure I-2). The run using acetate buffer had a first-order constant somewhat lower than the other runs in that set.

A plot of $\ln [\alpha\text{TNT}]$ remaining with time on samples subjected to sunlight gives qualitatively similar curves to those shown in figures I-1 and I-2, although the scatter of points is much greater in the sunlight-exposed samples. The increased scatter is thought to be due to variations in intensity of irradiation from natural sources.

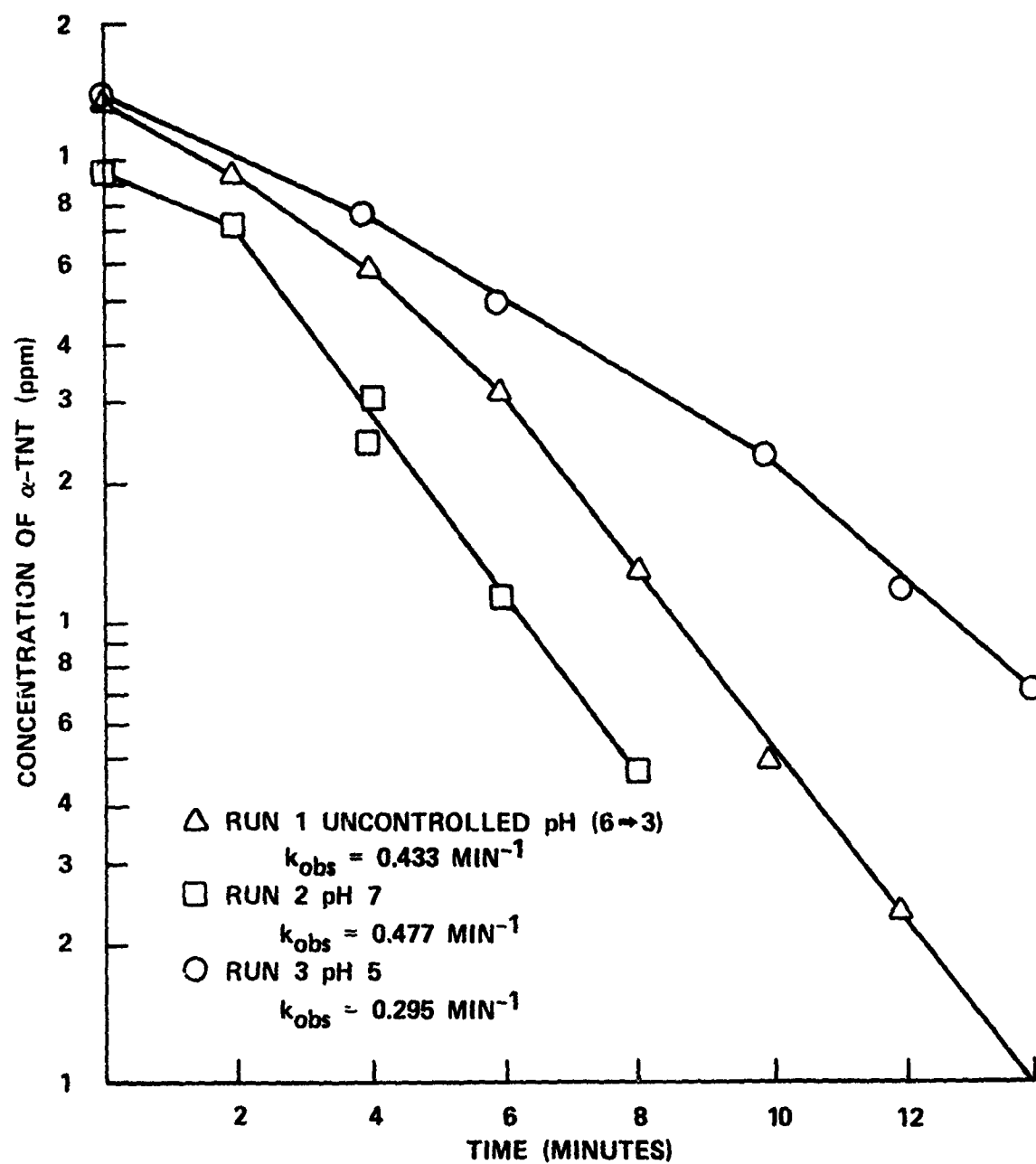


Figure I-1. Rate of Decomposition of α -TNT in Aqueous Solution
(Hanovia Lamp) – Set 1

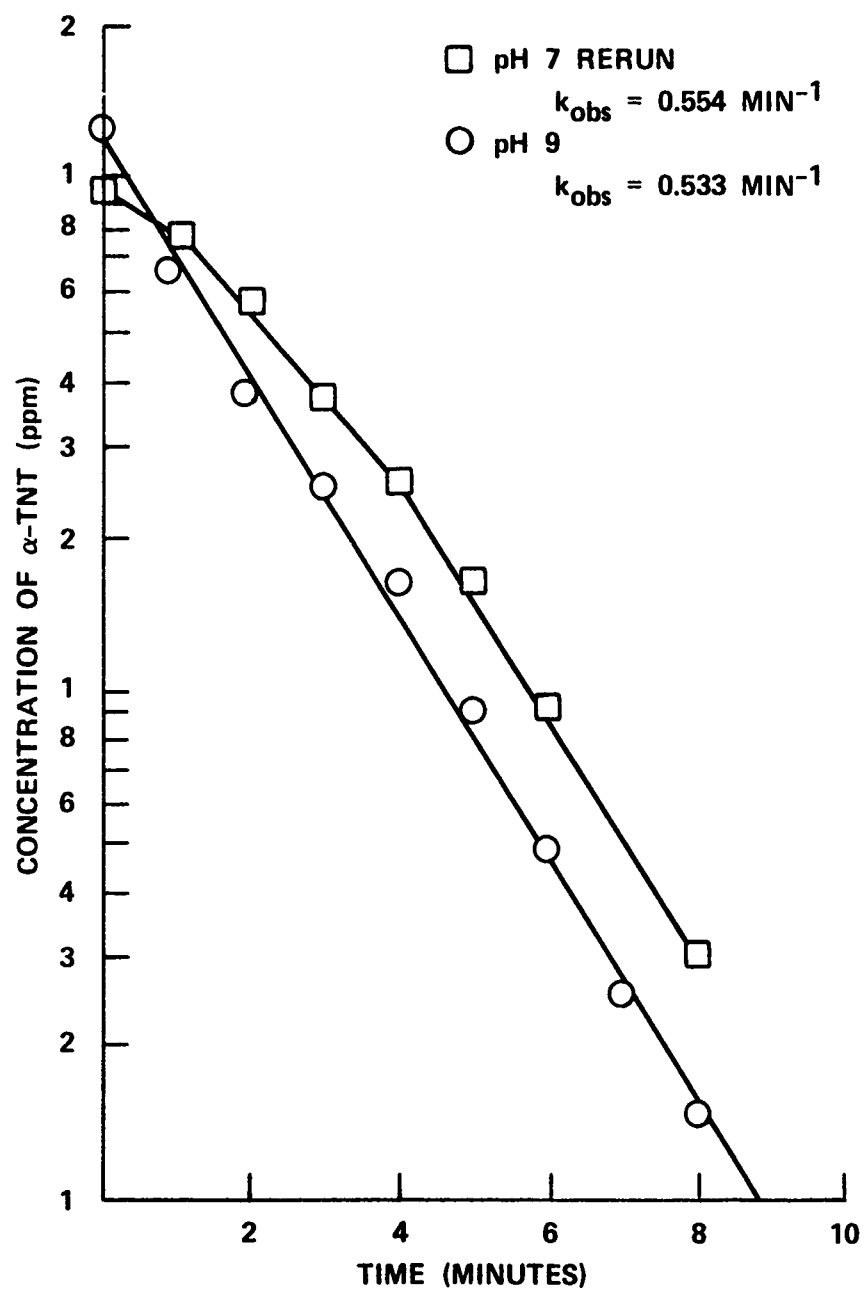


Figure I-2. Rate of Decomposition of α -TNT in Aqueous Solution (Hanovia Lamp) – Set 2

Although there is a qualitative similarity in the decomposition kinetics of α -TNT under artificial and natural sources of irradiation, the quantitative aspects are markedly dissimilar in that the decomposition rate of TNT under our experimental conditions is at least 1,000 times faster under the Hanovia lamp radiation than in natural sunlight. Thus compounds showing some stability to irradiation from the Hanovia lamp may be very stable under natural irradiative conditions.

Although varying conditions of light and temperature in the sunlight irradiation experiments precluded rigorous analysis of the data, there are some pertinent observations to be made. The shade and intensity of color were not a reliable indication of the extent of TNT photolysis. There was noticeable color after 10% of the α -TNT had reacted. Most of the color was found to have developed in the first 25% of the reaction and its shade was pH dependent. When the chloroform extracts of the sunlight-exposed solutions were examined by TLC, the decomposition of α -TNT appeared to be complex, with new materials appearing in an unpredictable manner.

b. Photolysis of RAAP Wastewater.

In the last three experiments listed in table I-14, aliquots of a sample of wastewater from the RAAP adjusted to and buffered at pH = 5, pH = 7, and pH = 9 were irradiated from 10 to 15 minutes with the Hanovia lamp. The GC analysis of chloroform extracts of the original water and the irradiated waters showed (see table I-15) (a) increasing proportions of 2,4-DNT and 2,6-DNT relative to α -TNT with irradiation at each pH, and (b) greater increases in the proportions of the DNTs relative to TNT with increasing pH, suggesting that TNT is more rapidly destroyed than the DNTs and that TNT is more subject to a pH effect than is DNT during irradiation. Furthermore, extrapolation of the effects of artificial-versus-natural irradiation on the kinetics of TNT transformation, together with the above observations, lead one to speculate that the DNTs may be sufficiently stable under conditions of natural irradiation to warrant their being considered as stable and long-lived compounds in wastewaters. The GC analysis showed also the existence of other compounds that appeared to be sunlight resistant.

c. Comparative Photolysis of TNT and DNT Isomers.

A brief study was made on the rate of decomposition of 2,4-DNT, 2,6-DNT, and several TNT isomers in aqueous solution (60 ppm) under irradiation by an unfiltered Hanovia lamp. Under these conditions, the 2,4,6-TNT, 2,4,5-TNT, 2,3,6-TNT, and 2,3,5-TNT isomers reacted about one order of magnitude more rapidly than the DNTs and 3,4,5-TNT (table I-16). It is noteworthy that the higher rates were observed with those compounds having three nitro groups, of which at least one is ortho to the methyl group.

d. Photolysis of Synthetic Red Water Condensate.

Red water, a byproduct of the sellite treatment in TNT manufacture, is concentrated for disposal by distilling off about 75% of the water. Along with the water, however, a number of nitroaromatics are also removed. At Volunteer Army Ammunition Plant (VAAP), this condensate is pumped to a holding tank to cool and then discharged into a nearby stream.

Table I-15. Photolysis of RAAP-CT-7/73 Wastewater; GC Analysis of Benzene Extracts

Component	Initial	Irradiated		
	pH = 2.2	pH = 5	pH = 7	pH = 9
		%		
2,6-DNT	2.0	1.6	2.5	3.5
2,4-DNT	13.0	20.4	41.9	60.0
RT = 149 min*	.2	.6	1.1	1.9
s-TNB	.6	3.2	3.8	6.5
α -TNT	82.9	72.4	45.5	1.0
RT = 259 min	.2	—	—	—
RT = 283 min	.1	—	—	—
RT = 342 min	—	—	—	4.5
RT = 406 min	.1	.47	1.5	4.6
RT = 502 min	.6	1.40	3.7	5.4

* Material with a retention time of 149 minutes.

Table I-16. Time to 50% Photolysis

Compound	Time
	min
2,4,6-TNT	2.0
2,4,5-TNT	3.0
2,3,6-TNT	1.5
2,3,5-TNT	2.0
3,4,5-TNT	15
2,4-DNT	25
2,6-DNT	20
3,5-DNT	*
1,3-DNB	*

* Negligible change in 165 minutes.

Four major components have been found⁸ in a sample of VAAP condensate: 1,3-dinitrobenzene (23.5 ppm), 2,5-dinitrotoluene (1.3 ppm), 2,4-dinitrotoluene (50.5 ppm), and 3,4-dinitrotoluene (8.6 ppm). A synthetic condensate, unbuffered (initial pH = 6.36), or adjusted to pH = 3 and pH = 8 with buffers, was irradiated for several hours with a Hanovia lamp equipped with a Pyrex filter. After 6 hours of irradiation, the pH of the unbuffered sample had dropped to 4.30.

Analysis for the four components in the different media was made at frequent intervals by gas chromatography (table I-17). Except for the 2,5-dinitrotoluene, which was more than 80% destroyed in 10 minutes in the unbuffered and pH = 8 solutions, and approximately 75% destroyed after 1 hour at pH = 3, the compounds were relatively stable even in the high-pH solution. For example, *m*-dinitrobenzene showed negligible decomposition after 2 hours in the unbuffered and pH = 3 solutions, and about 40% decomposition in the pH = 8 solution with no significant decomposition during the first 30 minutes of irradiation. The compound 2,4-DNT showed a 65% loss in unbuffered media, a 16% loss at pH = 3, and 87% loss at pH = 8 after 2 hours irradiation: the compound 3,5-DNT, exposed for the same time period, sustained a 25% loss in unbuffered, a 9% loss in pH = 3, and a 55% loss in pH = 8 media. For all compounds, the effect of pH on the photolysis rate appears to be similar to that found for TNT; namely, the rate increased with increasing pH.

5. Characteristics of the Colored Species in Pink Water.

Colored waters result from the irradiation of aqueous solutions of various aromatic nitro compounds; longer exposures or more intense radiation result in more intensive color. The irradiation of α -TNT is accompanied by production of acid. The pH of an aqueous solution originally containing 125 ppm of TNT ($5.6 \times 10^{-4}M$) dropped from pH of approximately 6 to pH = 3.5 after sunlight irradiation in a Pyrex vessel for approximately 1 month. The final TNT concentration was <1 ppm. To produce a solution with pH = 3.5 from a solution of $5.6 \times 10^{-4}M$ TNT would require that from 50% to 60% of the TNT be transformed into strong ($pK_a < 3.5$) water-soluble acids.

Definite coloration of the aqueous solution exposed to sunlight appeared within 1 day. The color had a maximum absorption of 510 nm. A sample that had been irradiated for 6 hours and had lost not more than 2 ppm of its TNT concentration had an optical density of 0.14 when viewed through a 1-cm cell. Assuming that the molecular weights of the colored bodies are close to that of TNT (approximately 200), their molar extinction coefficients are between 10^4 and 10^5 . This places them in a class with some of the very highly colored dyes.

The colored bodies are not entirely extracted into chloroform even at acidic pH levels, nor are they completely adsorbed onto carbon.¹⁶ They can be extracted with chloroform, however, if a phase transfer agent such as a tetrabutyl-ammonium salt is added to the aqueous solution to form an ion pair. The colored species are probably, therefore, anions of strong acids.¹⁷ The ion pairs formed between tetrabutylammonium salts and the colored species are very strongly bound; the anion could not be displaced from the ion pair with anions such as that of bromothymol blue. Moreover, it appears that the anions, if not already associated, tend to aggregate, polymerize, or form adducts or complexes. Three experiments supported the

Table I-17. Concentration Change of Condensate Constituents During Photolysis

Buffer	Time	Concentration			
		<i>m</i> -DNB	2,5-DNT	2,4-DNT	3,5-DNT
	min	ppm			
None	0	23.5	1.3	50.5	8.6
	10	22.0	.1	42.0	7.8
	20	21.6	—	37.0	7.3
	30	22.2	—	34.0	7.2
	60	22.4	—	26.0	7.0
	120	22.2	—	17.4	6.5
	150	21.9	—	16.0	6.4
pH=3	0	23.5	1.3	50.5	8.6
	10	23.0	.8	48.3	8.1
	20	22.3	.7	46.2	7.9
	30	22.6	.6	45.7	7.8
	60	23.1	.3	44.8	7.9
	120	23.2	—	42.2	7.8
	150	22.3	—	39.2	7.4
pH=8	0	23.5	1.3	50.5	8.6
	10	22.4	.2	43.6	7.7
	20	22.0	—	36.6	7.4
	30	22.6	—	31.7	7.4
	60	20.7	—	17.2	6.6
	120	13.8	—	6.5	3.9
	150	17.4	—	5.7	5.1

preceding statements: (a) A deep red solution with no apparent turbidity produced an orange colored filtrate when passed through an Amicon XM50 ultrafilter with a pore size of 33 Å. A red-brown deposit remained on the filter. The color in the filtrate could be extracted into chloroform after ion pairing with tetrabutylammonium ion. (b) A second sample, filtered through an Amicon UM05 ultrafilter with a pore size of 12 Å, produced a pale yellow filtrate and left a red-brown deposit on the filter. The deposits on the filter resisted all efforts at dissolution. Solutions of hydrochloric acid, tetrabutylammonium salts, and ammonium hydroxide were among those tried. Evaporation of the pale yellow filtrate produced a red solid that also resisted solution. (c) A third sample of pink water, after being filtered to remove any visible precipitate (0.8-μm filter), was centrifuged for 18 hours at 48,000 rpm. A yellow-to-red gradient formed in the cell.

Molecular weights in the range of 500 to 20,000 were estimated for the compounds.

6. XAD-8 Fractionation of TNT Water.

Many industrial problems involving a separation of toxic or hazardous organic impurities from water can be solved with nonionic polymeric adsorbents.¹⁸ Amberlite XAD-8,* an acrylic ester with intermediate polarity, offers a promising separation technique for photochemical products found in TNT wastewater discharges. These materials are not easily extracted with organic solvents without the use of complexing agents such as TBAS, which binds so strongly that subsequent analysis of the extracts is further complicated. After a column separation using XAD-8, the solvents can be evaporated easily from the various fractions and the residues can be reconstituted in organic solvents for further analysis.

Amberlite XAD-8 was equilibrated with triple-distilled water for several hours and packed in a 1/2-inch glass column to a bed height of 17-3/4 inches. The column was fitted with a Chromatronix SV 8031 sample injection valve with a 5-ml sample loop. A gradient of water and acetonitrile was delivered at a combined flow rate of 175 ml/hr (±2%) with an Isco Dialagrad model 382 programmed pumping system. The gradient was programmed through 11 stations (dials on the Dialagrad), to deliver 0, 2.5, 5, 7.5, 10, 15, 20, 30, 50, 75, and 100 percent of acetonitrile, over a 2-hour program. The water and acetonitrile (spectro grade) were degassed prior to use. The effluent was monitored at 2,700 Å with a Beckman model DB spectrophotometer that was fitted with a 0.25-ml flow microcell having a light path of 1.0 cm, and a strip chart recorder. As the peaks appeared on the recorder, the outlet tube of the column was manually positioned over a set of numbered screw-top tubes.

Samples of laboratory-irradiated TNT, JAAP-PF-8/73, and JAAP-PF-12/74 wastewaters were chromatographed using this system. A typical elution profile with the solvent gradient superimposed is shown in figure I-3.

Several portions of JAAP-PF wastewater (after removal of the neutral fraction by extraction with chloroform) were fractionated on XAD-8 and the corresponding fractions were pooled, evaporated to dryness, and dissolved in methanol. The methanol solutions were applied

* Trademark Rohm and Hass, Inc., Philadelphia, Pennsylvania.

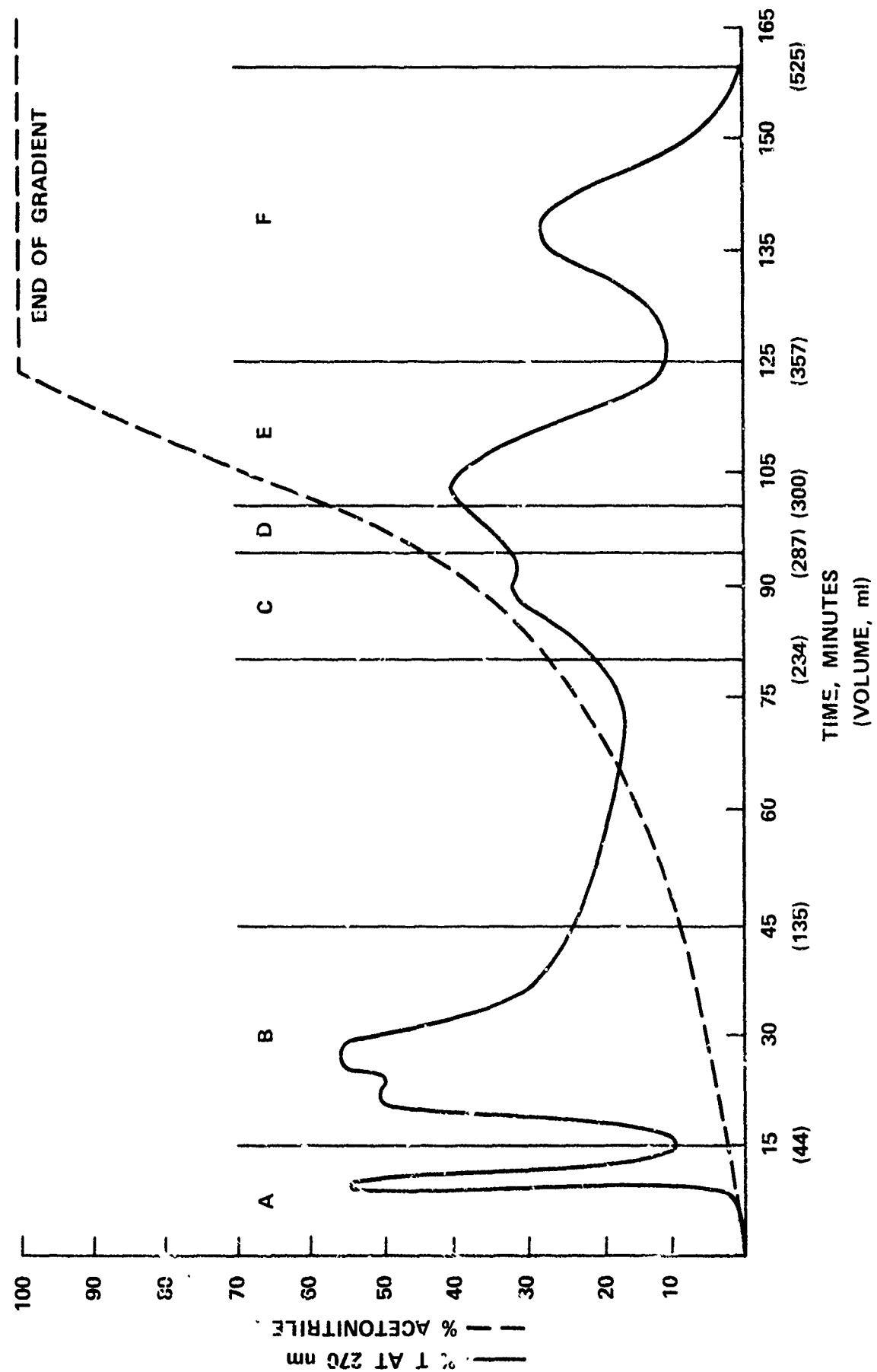


Figure I-3. Chromatogram of JAAP-FF-8/73 on XAD-8 Using a Water-Acetonitrile Gradient

to silica gel TLC plates and developed with benzene-ether-ethanol (50:30:20). Spots of an ether (pH = 1) extract of the same wastewater sample were included on the chromatoplates. Results of TLC are summarized in table I-18.

The components of the ether extract could be correlated only in part with the several fractions from XAD-8. A large part of fractions A to E did not migrate in the TLC solvent; this origin material may be strongly polar, as suggested by the 2,6-dichloroindophenol test for acids, or aggregates of high molecular weight. The TLC origin material of fraction F differed from that of the other fractions; it gave a negative test with 2,6-dichloroindophenol and a positive test with $\text{FeCl}_3\text{-K}_3\text{Fe}(\text{CN})_6$, suggesting a phenolic compound.

The chromatogram of fraction B had four major spots ($hR_f = 36, 42, 70$, and 76); fraction C had four major spots ($hR_f = 10$ to $25, 26$ to $40, 46$, and 52); and fraction F had three major spots ($hR_f = 70, 78$, and 80). Absence of a corresponding TLC spot in the intervening XAD-8 fractions and differing reactions with the spray reagents demonstrate that chromatography on XAD-8 resin separates compounds not resolvable by the TLC systems.

Obviously the potential of this approach has not been fully realized. It appears, however, from these exploratory experiments that pink water can be preparatively separated on XAD-8 resin into fractions for further study of the color body constituents.

7. Lyophilization and Reconstitution Studies.

For chronic toxicological studies, it is necessary to have wastewater samples in which the compounds are invariant with time. Lyophilization (freeze-drying) is a gentle, easily performed method for isolating the total solids in an aqueous system. To ascertain whether lyophilized solids could be redissolved to produce solutions equivalent to the original wastewaters, samples characterized by GC, TLC, and HPLC were lyophilized to dryness, reconstituted (by adding the original volume of water to the solids), and again characterized. The lyophilized solids were generally of low density and tended to be electrostatic.

a. Lyophilization and Reconstitution of Wastewater Samples.

Some properties of five lyophilized AAP wastewater samples are listed in table I-19.

Although the lyophilized and reconstituted waters were almost identical with the original solutions, there were some slight differences. The GC of one lyophilized sample (prepared from JAAP-PF-8/73 wastes) showed a loss of two compounds, both present in extremely small quantities in the original sample; there was complete agreement between the unlyophilized and lyophilized samples by both LC and TLC on the neutral as well as the ion-pair fractions. A second sample, from LAAP-BG-1-8/73, had but one minor difference, a new GC peak (0.5% of total area) at 667 seconds on the lyophilized sample.

Table I-18. Spot Colors for the TLC Analysis for Fractions of JAAP-PF-2/73,
TLC Solvent: Benzene-Ether-Ethanol (50:30:20)

hR_f	XAD-8 fractions						Ether extract
	A	B	C	D	E	F	
80	-	-	-	-	(Very weak) pink	(Moderate-strong) red ^{a,b}	-
78	-	-	-	-	-	(Weak) yellow	-
77	-	-	(Very weak) pink	-	(Very weak) yellow	-	(Moderate) Red-brown ^b
76	-	(Moderate) pink	-	-	-	-	-
72	-	-	(Very weak) yellow	-	-	-	-
70	-	(Weak) yellow	-	-	-	(Moderate-strong) yellow ^b	-
69	-	-	-	-	-	-	(Strong) orange-tan ^{a,b,c}
67	-	-	-	-	(Very weak) pink	-	-
61	-	-	-	-	-	-	(Moderate) pink-purple
59	-	-	-	(Fluorescent) ^d	-	-	-
53	-	-	-	(Fluorescent) ^e	-	-	-
52	-	-	(Weak) yellow ^{d,e}	-	-	-	-
51	-	-	-	-	-	-	(Weak) lavender
48	-	-	-	Yellow (fluorescent)	-	-	-
46	-	-	(Moderate) yellow	-	-	-	-
43	-	-	-	-	-	-	(Strong) rose
42	-	(Weak) pink	-	-	-	-	-
38	-	-	-	-	-	-	(Strong) yellow-tan
36	-	(Weak-moderate) yellow	-	-	-	-	-
33	-	-	-	-	-	-	(Weak) pink-lavender
30	-	-	-	-	-	-	(Moderate) purple-brown
29	-	-	-	-	(Weak) yellow	-	-
26 ^f	-	-	(Weak-moderate) yellow ^a	-	-	-	-
25	-	-	-	-	-	-	(Moderate) tan ^{a,b}
11	-	-	-	-	-	-	(Strong) purple-brown
10 ^g	-	-	(Weak-moderate) yellow	-	-	-	-
6	-	(Weak) tan	(Weak) tan	-	(Weak) pink-tan	-	(Moderate) red-brown
2	-	(Weak) tan	(Weak) tan	-	-	-	-
0	(Strong) brown ^c	(Moderate-strong) brown ^c	(Strong) brown ^c	(Weak-moderate) brown ^c	(Moderate-strong) brown ^c	(Weak) tan ^b	(Dark) brown ^{b,c}

^a Color with modified Ehrlich's reagent as detector reagent is pink.

^b Color with $\text{FeCl}_3\text{-K}_3\text{Fe(CN)}_6$ as detector reagent is blue.

^c Color with 2,6-dichloroindophenol as detector reagent is dark pink.

^d Color with modified Ehrlich's reagent as detector reagent is yellow.

^e Color with 2,6-dichloroindophenol as detector reagent is dark blue.

^f The color given extends over the range of hR_f values 26 to 40.

^g The color given extends over the range of hR_f values 10 to 25.

Table I-19. Properties of Five Lyophilized AAP Wastewater Samples

Sample	Total solids	Ash content*	Final appearance
	mg/l	%	
JAAP-PF-8/73	1200	18.1	Red-brown powder
LAAP-BG-1-8/73	835	39.5	Dark red-brown powder
HAAP-S-9/73	250	49.8	Fine orange-tan powder
RAAP-ST-1/74	900	75.0	Fine light tan powder
JAAP-PF-12/74	1572	67.9	Red-brown powder

* A measure of the inorganic material in these samples.

The discrepancies with the RAAP samples were several. By GC analysis, there was a loss in the lyophilized sample of a compound that comprised 0.5% of the total area in the original. A compound appeared among the neutrals in the lyophilized sample by LC analysis and was absent in the original wastewater. Two important differences were seen by TLC: at $hR_f = 45$ there was a yellow color of very low intensity (after EDA-DMSO spray) in the original but an intense purple color in the lyophilized sample; a spot fluorescent under ultraviolet irradiation at $hR_f = 12$ in the original was not seen in the reconstituted sample.

In an attempt to explain the formation of a new compound at $hR_f = 45$ (developed with S2 solvent), a mixture of equal parts of 60-ppm solutions of 2,4,6-TNT and 1,3,5-TNB was freeze-dried. When the residue was dissolved in chloroform and used for TLC analysis the lyophilized mixture gave two new spots. The more prominent spot corresponded in hR_f value and color reaction to the $hR_f = 45$ spot, indicating that interaction between two compounds normally found in wastes can occur during lyophilization.

The changes in composition attributable to the lyophilization process were few and minor, however, when compared with the changes noted by TLC analysis of wastewater samples that had been allowed to sit in the laboratory for several months and retested. These differences, which appeared in both the neutral and ionic fractions, were due to the formation of new compounds.

Some differences in chemical composition of the initial wastewaters and the lyophilized reconstituted samples were expected. Concentration techniques such as lyophilization could be expected to accelerate agglomeration of some of the water-soluble compounds and to increase the rates of reaction among many of the neutrals. In fact, coupling products have been observed in purified TNT from the continuous process.² These include 2,2',4,4',6,6'-hexanitrobibenzyl (coupling of two 2,4,6-TNT molecules); 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane (coupling of 2,4,6-TNT and 2,4,5-TNT); and a third component, presumably the 2,3,5-TNT and 2,4,6-TNT coupling product. Also sometimes observed in the continuous process is 3,3',5,5'-tetra-nitroazoxybenzene, produced from reductive coupling of 1,3,5-trinitrobenzene or by decarboxylation of carboxy white compound.

b. Lyophilization and Reconstitution of Yellow Water.

Whereas most of the wastewater samples were in the pH = 6 to 8 range, some wastes were strongly acidic from yellow water, which consists of weak spent acids (nitric and sulfuric acid mixtures) and wash waters from TNT manufacture. To test whether problems would be encountered in lyophilization and reconstitution of acidic wastes, a saturated aqueous TNT solution was prepared and adjusted to pH = 2.5 with a mixture of nitric and sulfuric acids (1:1 by volume). An aliquot of this synthetic yellow water was lyophilized, reconstituted, and analyzed.

Benzene, instead of chloroform, was used for extraction of the neutral fraction in the yellow water experiment; we had previously shown, however, that extracts with benzene or chloroform are indistinguishable. As a further check, aliquots of the aqueous phases (after benzene extraction) were analyzed by the alternative procedure that uses TLC of ether extracts of pH = 1 solutions, as well as by ion-pair extraction with chloroform.

TNT accounted for most of the material (estimated >95%) in the control and in the lyophilized and reconstituted benzene extracts as analyzed by GC, LC, and TLC. When small samples were applied to the TLC plate and S1 solvent used to develop the chromatogram, only one other spot was found ($hR_f = 40$, probably 2,4,6-trinitrobenzaldehyde). Since an identical chromatogram was given by a sample of the TNT used to prepare the yellow water solutions, the minor fractions found on thin-layer chromatograms were probably impurities in the TNT. The lyophilized sample gave deeper pink spots than the control at $hR_f = 34$ to 37 and at the application area; in other respects, they appeared to be identical.

TBAS-chloroform extracted very little additional material from the aqueous phase. A single distinct TLC spot was found at $hR_f = 55$, blue with EDA-DMSO, in both the control and lyophilized samples; and a broad, diffuse area at $hR_f = 45$ to 50, faint tan with EDA-DMSO. No material remained at the application area of the TLC plate. Ether extracts of the aqueous phases each had only a trace of material, at $hR_f = 65$.

In order to reinforce conclusions regarding the effects, if any, of lyophilization and reconstitution of synthetic yellow water, the experiment was repeated with photolyzed solutions. Any differences between the control and reconstituted samples would be magnified by different photolytic behavior. Aliquots of the pH = 2.5 control and lyophilized solutions were irradiated for 4 hours with a Hanovia lamp with Pyrex filter, and reanalyzed.

The two photolyzed samples appeared to be very similar, but not identical. Very little material was extracted by benzene. GC analysis showed the appearance of a new peak (at 515 sec) after lyophilization, with corresponding diminution of a peak at 310 sec, while a peak at 417 sec was unchanged. Thin-layer chromatograms of the two benzene extracts, however, appeared identical in relative spot intensity as well as hR_f values and color reaction with EDA.

Ion-pair extracts of the aqueous phases (after benzene) of both photolyzed solutions gave thin-layer chromatograms that differed slightly in appearance, but identity of fractions was readily determined by comparing color reaction with EDA as well as spot shapes and hR_f values.

Each chromatogram showed 12 separated components. Differences in R_f values between samples probably reflected concentration differences of the various compounds. A large portion of the sample remained, however, as dark brown material at the application area. Thin-layer chromatograms of the ether extracts were relatively independent of concentration and better resolved than the ion-pair extracts. The photolyzed control gave 19 spots of varying intensity, and the reconstituted sample showed the same 19 components plus one additional faint spot.

Again, as in the wastewater lyophilization experiment, only minor differences were found between the control sample and lyophilized and reconstituted samples.

III. DISCUSSION.

The objective of this study was to provide information that would assist the Surgeon General in the design of appropriate toxicological studies for the purpose of establishing water quality control guidelines or standards for wastewaters from TNT production and loading facilities. Ideally, for toxicological evaluation, one should know the identity of the individual compounds constituting the pollutants. With knowledge of the individual and collective effects of the pollutants, and the quantity of each of the compounds in the waste discharges, one can assign waste discharge limits.

It has been determined that the number and structure of the contaminants in wastewaters will vary from plant to plant, and within a plant will vary from time to time, so that it becomes meaningless to set standards from toxicological evaluation of any individual sample.

In many cases the history of the waste sample (source, sampling site, pretreatment) will limit the compounds that must be considered for identification of unknowns. For example, wastes from a LAP plant could very likely contain RDX or HMX, not found in a TNT-manufacturing plant, and would have only the TNT process materials that were in the finished TNT or derived from TNT and its impurities. Condensate from red water concentration, on the other hand, consists of volatile or steam-volatile pyrolysis products and thermally stable compounds.

Because of the known variation in physiological activity shown by different compounds, minor impurities in wastewaters cannot be arbitrarily eliminated from toxicological and environmental impact assessment. However, in priority of testing, it would appear advisable to spend minimum effort on compounds that are both low in concentration and unstable to light.

These preliminary studies indicate that the rate of photolytic decomposition of nitrated toluenes will be dependent upon factors such as intensity of illumination, pH of the aqueous solution, and the structure of the nitro compound. Concerning the structure, our studies suggest that there will be marked differences in the susceptibilities to photolytic decomposition of the compounds found in wastewaters. Under the same conditions of pH and intensity of illumination, it appears as if α -TNT (and other trinitrotoluenes having at least one ortho-nitro group) decompose much more rapidly than some of the dinitrotoluenes, e.g., 2,4-dinitrotoluene and 2,6-dinitrotoluene. If, as suggested by our studies using natural light, the

decomposition of TNT can be quite slow under real conditions, then, by extrapolation, some dinitrotoluenes (and probably mononitrotoluenes) and other nitro compounds, such as dinitrobenzenes and trinitrobenzenes, should be considered as stable compounds. Thus, a determination of the toxicological and environmental impact of these types of compounds is indicated.

Prominent among the compounds that have been identified in the aqueous fraction (not extractable with chloroform or benzene) are variously substituted tetranitroazoxybenzenes and azobenzenes. The substance 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene (white compound) and the related mono-carboxy compound have been reported both as byproducts in TNT manufacture⁵ and as TNT photolysis products.⁷ Many of the TLC-separated spots that give purple colors with ethylenediamine probably belong to this class of compounds. Other identified aqueous-phase compounds in pink water are the dinitrobenzoic and trinitrobenzoic acids. The compound 2,4,6-trinitrobenzoic acid rapidly decarboxylates to 1,3,5-trinitrobenzene,¹⁹ but 2-amino-4,6-dinitrobenzoic acid is found as a major photolysis product of TNT.⁷ The substituted azobenzenes and azoxybenzenes, and the polynitroaromatic carboxylic acids should be considered as candidate materials for toxicological evaluation.

Not to be overlooked in toxicological evaluation of wastes is whether the waste components themselves or compounds from the waste components have an environmental impact. Effluent chemicals can be transformed by hydrolysis, oxidation, irradiation, or interaction with other waste components, either during their storage period prior to discharge into the waterways or during their existence in the waterways. Also, one should consider and evaluate the effect of chlorination on the waste compounds (and their transformation products), since practically all public drinking water in the United States is chlorinated.

The results of these studies suggest plant treatment procedures to minimize the environmental pollution problem. The photolytic reaction is pH dependent and extremely slow at low pH levels. To retard the photolytic transformation, it would appear desirable to maintain an acidic pH in the storage of wastes.

The use of carbon for treatment of TNT wastes has been in existence for some time.²⁰ Synthetic polymeric adsorbents are currently under evaluation as a substitute for carbon;¹⁶ studies on biodegradation, by bacteria of explosives such as TNT, followed by denitrification of the explosives by anaerobic bacteria to convert nitrates and nitrites to elemental nitrogen, are being carried out.²¹

A combination of the three processes for treatment of TNT wastes, in the sequence of carbon adsorption, ion exchange, and bacterial treatment seems to be indicated. Removal of neutrals (including, in part, acids such as trinitrophenol and trinitrobenzoic acid) can be effected by carbon adsorption. Recovery of the adsorbed materials is considered feasible.¹ The small quantity of organic anions that escape carbon adsorption can be removed from water by use of ion-exchange resin (in the nitrate form). The effluent from the ion-exchange treatment can be neutralized and biologically treated to reduce the nitrate and nitrite ion concentrations to acceptable levels. The ion-exchange resin may not be regenerable; however, the quantity of material that will be adsorbed will be very small if the carbon adsorption process is very efficient.

IV. CONCLUSIONS.

Studies were made on TNT loading and manufacturing plant wastewaters that become colored when exposed to sunlight (pink waters) and on laboratory-irradiated synthetic solutions of nitroaromatic compounds.

Chromatographic techniques were found to be extremely valuable for separation and identification of complex mixtures. Methods used to determine identity of waste components included complementary chromatographic techniques (GC, TLC, HPLC) and specific detection reactions. The addition of phase-transfer compounds such as tetrabutylammonium salts permitted the extraction of hydrophilic impurities into chloroform. Propylene glycol, added to organic solvent extracts of wastewaters prior to concentration, ameliorated further handling of the residues.

The composition of TNT wastewaters from different sampling sites was variable, and the composition of a specific waste stream varied significantly with time. The TNT wastewaters contained a complex mixture of organic materials with a wide range of molecular weights, solubility, and polarity. There were few materials that were common to all wastes.

Evidence was found that the colored bodies in pink water, including those produced by α -TNT photolysis, have high extinction coefficients, are largely anionic, and display the characteristics of molecular aggregates. The shade of color developed upon photolysis of a waste sample was pH dependent, and the rate of photolysis of waste samples was much slower at low pH.

Unstable compounds are converted to decomposition products either during storage or after discharge into the waterways; stable compounds remain in the wastewaters. In studies of relative rates of photolysis of trinitrotoluene and dinitrotoluene isomers, compounds not possessing a nitro group ortho to a methyl group were more stable, and DNTs were more stable than TNTs. All rates were much slower at low pH (<5).

Lyophilization (freeze-drying) was examined as a solution to the problem of uniformity and storage stability of wastewater samples for extended biological experiments. In extensive studies only minor differences in composition were found between the control samples and lyophilized and reconstituted wastewater samples.

Preliminary experiments indicated that aqueous waste can be fractionated, without prior treatment, on an XAD-8 resin column to yield fractions suitable for further studies.

A continuation program should include toxicity determinations of compounds that were found to be present in most wastes and that were relatively stable to photolysis.

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ENVIRONMENTAL QUALITY STANDARDS RESEARCH ON WASTEWATERS OF
ARMY AMMUNITION PLANTS

PART II. NITROGLYCERINE WASTEWATER STUDIES

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PART II. NITROGLYCERINE WASTEWATER STUDIES

I. INTRODUCTION.

Glycerine trinitrate or *nitroglycerine* (trinitroglycerine, TNG) is manufactured at United States Army GOCO Plants at Radford, Virginia (RAAP) and at the Badger Army Ammunition Plant (BAAP) in Baraboo, Wisconsin. Although both plants produce TNG by the nitration of glycerine, RAAP used a continuous process, and it is the wastewater from this process on which the analytical procedures described in this report were developed. The wastewater from the BAAP batch process would not be expected to be radically different from that from RAAP, but analytical development using this water was rejected for two reasons: (a) all wastewater is channeled into a single discharge pipe so that the composition of the discharge is dependent upon the part of the batch operation that is in progress and (b) the batch production of TNG was discontinued in calendar year 1975.

As illustrated in figure II-A-1, appendix, part II, there are two waste streams from the RAAP operation. The first stream combines aqueous sodium carbonate and water washes as they emerge from the separators. These waters are discharged into a large baffle tank (figure II-A-2). In this tank, water-insoluble materials are allowed to settle out or rise to the surface (depending on density). An oily liquid that settles to the bottom consists primarily of TNG, glyceryldinitrates (dinitroglycerines, DNG's), and glycerylmononitrates (mononitroglycerines, MNG's). This liquid is drained and returned to the nitrator. The particulate and oil material on the surface is skimmed off and sent to the incinerator. The overflow from this tank passes through a second tank for similar treatment. It should be noted that both of these tanks are in buildings and thus protected from the weather. The overflow from the second tank is channeled through a long (200-yard) metal-lined trough. This trough is joined at about its midpoint by another that carries cooling water from the spent-acid recovery tanks. From there, the water is discharged directly into the New River. The water samples at the third tank will be referred to as RAAP-NG-W. An earlier sample taken from this waste line for preliminary studies will be referred to as RAAP-NG-Wa.

The finished TNG is piped to a pair of storage tanks where it is held under a layer of fresh water. Since this water is continually replaced, it functions in essence as a final wash and forms the second waste stream. This water is passed through two baffle tanks and then discharged into the New River. Sample RAAP-NG-S was taken at the overflow of the second tank.

II. ANALYTICAL METHODS.

A. Carbon Analysis.

An Oceanography International carbon analyzer was used to determine the carbon in the RAAP-NG wastewaters. Carbonate (inorganic carbon) is determined by injecting a sample into phosphoric acid sealed under a nitrogen stream. The evolved CO_2 is carried by the nitrogen through an infrared (IR) detection system whose electronically integrated signal is proportional

to the original carbonate level. The total carbon level is determined by combustion of the sample on a hot filament in an oxygen atmosphere. The CO_2 produced is measured by the same IR apparatus. Organic carbon is the difference between total and inorganic carbon. It is essential that the measurements be made as close to the same time as possible and that no pH change occur if dilution is required.

B. Nitrate Analysis.

Determination of inorganic nitrate levels was made with an Orion model 92-07 specific nitrate electrode. The pH of the samples was reduced to a value between 6.5 and 7.5 using Dowex 50W-X2 ion-exchange resin (H⁺ form), and the sample was then boiled to remove the remaining dissolved CO_2 . After cooling, the original volume was reestablished with distilled water or was diluted 1:10 if the nitrate concentration was high.

Before the nitric ester groups in the wastewater could be determined, it was first necessary to remove the inorganic nitrate ion. To accomplish this, a sample of wastewater was adjusted to pH = 7 with Dowex 50W-X2 ion-exchange resin and heated to boiling to remove CO_2 . A 10.0-ml aliquot of the prepared sample was chromatographed on a 2.3- by 35.5-cm column of Bio-Rad ion retardation resin. This resin, eluted with distilled water, binds and retards the passage of inorganic ions, but allows organic molecules, including those with formal charges, to pass unhindered. The elution data supplied by the manufacturer was used to determine the fraction containing the organics (0 to 300 ml). This fraction was lyophilized, resulting in a thin film of material on the wall of the flask. The material was dissolved in approximately 5 ml of 5N NaOH and allowed to stand for 30 to 60 minutes. The solution was diluted to 100.0 ml and the pH adjusted to approximately 7 with Dowex 50W-X2. The nitrate liberated by hydrolysis was measured with the specific ion electrode. Inasmuch as hydroxide attack also liberates nitrate ion, the relationship between nitrate yield and TNG concentration is uncertain.

C. Gas Chromatography (GC).

To prepare the samples for GC analysis, 100 ml of wastewater was shell frozen in a round-bottom flask and lyophilized. The solid material was washed with five 50-ml portions of diethyl ether. The pooled ether washes were evaporated at room temperature to approximately 0.5 ml.

The analyses of the ether extracts of lyophilized NG wastewater were performed on a Hewlett-Packard 5830A gas chromatograph that has built-in electronic integration and normalization capability. This instrument was fitted with a 6-foot by 2-mm (ID) glass column of 5% UCW-98 on 100/120-mesh Chromosorb W. A flame ionization detector was used with the helium carrier flowing at 20 ml/min. Samples were all 1 μl and injected directly on the column. The injector was maintained at 160°C, the detector at 200°C, and the oven was programmed from 60°C to 150°C at 5°C per minute after a 2-minute isothermal postinjection period. All runs were done in at least duplicate and standards were used frequently to monitor for changes in column performance.

Chromatograms of ether solutions of standard materials, 1-MNG, 2-MNG, and 1,3-DNG (supplied by Naval Ordnance Laboratory), and TNG diluted with β -lactose (DuPont), each showed single major peaks (>85%) along with a number of impurities (table II-1). One curious observation was that all four standards had an impurity with a retention time (RT) of 3.7 to 4.0 minutes.

D. Irradiation of Wastewater.

Aliquots of about 500 ml each were exposed to six hours of irradiation from a 400-watt Hanovia Hg arc lamp in an Ace Glass photolysis apparatus. Each sample was exposed to both unfiltered light and light filtered through a Pyrex sleeve. After irradiation, the pH of each sample was measured, the ultraviolet and visible spectra were recorded, and the samples were prepared for GC analysis as previously described.

E. Thin-Layer Chromatography.

The wastewater samples were prepared for TLC by partition chromatography on Johns-Manville Celite 545. Typically, 10 ml of aqueous sample in a 250-ml beaker was thoroughly mixed with 10 grams of reagent-grade Celite 545, using a stainless steel spatula. Two ml of dry ethyl acetate was added and thoroughly mixed in. A glass column, 20 nm in diameter, having a fritted glass support and Teflon stopcock, was packed by adding the mixture in four portions with tamping (19-mm diameter stainless steel tamper) after each addition. The tamper, spatula, beaker, and funnel were scrubbed with a small portion of glass wool that was then tamped onto the column. The column was eluted with ethyl acetate, previously saturated with water; 10 ml was first used to rinse the beaker and the sides of the glass column, and as the meniscus entered the glass wool plug, an additional 40 ml was added to the column. Twenty ml of the eluate was collected at a rate of about 2 ml/min. The eluate was dried with anhydrous sodium carbonate and filtered through glass wool.

Recoveries of TNG, MNG, and 1,3-DNG, and various mixtures of these were greater than 95% by this method. The compounds separated by TLC of the eluate matched the standards, including the minor components, found in the 1,3-DNG sample. Potassium nitrate at a concentration of 300 ppm NO_3^- did not contribute to nitrate in the eluate.

Thin-layer plates used were 5-by 20-cm silica gel analytical plates (Quantum Industries), types LQ, LQF, LQD, LQDF, and Q5. The LQ type has an inert, pre-adsorbent spotting area at the bottom of the plate; the LQD type is additionally divided into four channels.

All chromatographs were developed by the ascending technique in tightly closed, saturated cylinders for a distance of 4 inches, using 25 ml of developing solvent. Nitrate esters were visualized by spraying with a 1% alcoholic solution of diphenylamine (DPA), followed by irradiation with strong ultraviolet light for 1 to 2 minutes. Some plates were sprayed with a 0.5% solution of 2,4-dinitrophenylhydrazine (DNPH) in 2N HCl as a test for carbonyl groups.

Table II-1. GC Retention Times of Nitroglycerine Standards

RT	Compound			
	TNG	1,3-DNG	1-MNG	2-MNG
min				
1.01	—	X	—	—
1.05	X	—	—	—
1.21	X	—	—	—
1.99	X	—	—	—
3.70	X	—	—	—
3.81	—	X	—	—
3.87	—	—	—	X
3.95	—	—	X	—
10.99	—	X	—	—
13.1	—	X	—	—
13.37*	—	—	—	X
13.42	—	X	—	—
13.72	—	X	—	—
13.73*	—	—	X	—
14.50	—	X	—	—
14.91	—	X	—	—
16.35	—	X	—	—
16.87	—	—	—	X
17.19	X	—	—	—
17.22*	—	X	—	—
18.65*	X	—	—	—
27.50	—	X	—	—

* Major peak (>85% of total peak area).

The NG standards used as GC standards were subjected to TLC; several solvent systems were used for development of the chromatograms. The most suitable solvent systems were the three shown in table II-2, and these were used for the wastewater extracts. Note that none of these solvents would resolve the MNG isomers.

III. RESULTS.

The results of the carbon and nitrate analyses on RAAP-NG-W and RAAP-NG-S are shown in table II-3. To facilitate interpretation, the data are given in ppm and molar concentration, except for inorganic carbon, for which the data are given in terms of weight of sodium carbonate per liter.

The total carbon analyzer was used to determine the efficiency of the ether extractions. A 100-ml sample of wastewater was lyophilized and extracted as above. The ether was allowed to evaporate completely and the residue dissolved in 100 ml of carbonate-free water (so that the organic carbon was the total carbon). The organic carbon found in the RAAP-NG-W and RAAP-NG-S samples is given in table II-4.

The gas chromatogram from the ether extract of RAAP-NG-W showed 37 components of which 9 had areas $\geq 1\%$ of the total peak area, and accounted for 91% of the total peak area. When RAAP-NG-W was neutralized (to pH = 7 using Dowex 50W-X2), lyophilized, and extracted, GC showed only 28 peaks of which 9 were $\geq 84\%$. As table II-5 shows, these nine peaks are not the same. In fact, only four appear to be present in both preparations: RTs 0.98 and 1.02, 3.78 and 3.92, 13.03 and 13.31, 29.43 and 29.43. Although the correspondence of the 13.03 and 13.31 pair might be questionable, both peaks were strong, isolated, and showed similar tailing characteristics.

Similar chromatograms were obtained for the RAAP-NG-S sample (table II-6). In this case, 42 peaks were observed in the untreated sample. Of these, ten were $\geq 1\%$ of total area and summed to 90% of total area. After neutralization, 59 peaks were obtained of which 13 were $\geq 1\%$ total area and totaled 90% of the total area. As can be seen in the table, six peaks could be correlated: RTs 3.63 and 3.81, 3.88 and 3.97, 5.65 and 5.08, 6.15 and 6.16, 25.31 and 25.44, 29.63 and 29.84.

The pH of RAAP-NG-W and RAAP-NG-S before and after irradiation is given in table II-7. The UV-Vis spectra are shown in figures II-A-3, II-A-4, and II-A-5. The retention times of the major GC peaks ($\geq 1\%$ of total peak area) are listed in tables II-8 and II-9.

TLC of the ethyl acetate extract of RAAP-NG-Wa developed with the three solvents in table II-2 showed spots with R_f values corresponding to TNG, 1,3-DNG, and the MNGs. A second sample of this wastewater was extracted with chloroform and then chromatographed with chloroform. A DPA-positive spot observed at $R_f = 0.51$ was presumably TNG. A second spot at $R_f = 0.64$ was negative to DPA but did quench fluorescence. This spot produced a light yellow color with DNPH spray.

Table II-2. R_f Values of NG Standards on Silica Gel TLC Plates
With Various Solvent Systems

Solvent system	TNG	1,3-DNG	MNG
Benzene-ethyl acetate (2:1)	.64	.56	.13
Benzene-ethyl acetate-acetic acid (16:4:1)	.65	.57	.18
Chloroform-toluene (85:15)	.62	.19	.04

Table II-3. Carbon and Nitrate Analyses of NG Wastewaters

Substance	RAAP-NG-W equivalent	RAAP-NG-S equivalent
	ppm	ppm
Inorganic carbon	1,283 12 gm $\text{Na}_2\text{CO}_3/\ell$	1,907 18 gm $\text{Na}_2\text{CO}_3/\ell$
Organic carbon	67 .0056 M	268 .022 M
Inorganic nitrate	22,300 .36 M	1,350 .022 M
Organic nitrate	38.5 6.2×10^{-4} M	10.5 1.7×10^{-4} M

Table II-4. Efficiency of Ether Extraction of Lyophilized NG Wastewater

Sample	Total organic carbon	Extracted organic carbon	Percent extracted
	ppm	ppm	
RAAP-NG-W	67	29	43
RAAP-NG-S	268	30	11

Table II-5. GC Data for Ether Extracts of Lyophilized RAAP-NG-W

Retention time	Peak area for untreated sample	Peak area for neutralized sample
min	% of total	% of total
0.98	23.9	—
1.02	—	1.8
1.41	1.7	*
1.67	1.1	*
2.05	**	1.9
2.45	*	1.1
3.52	39.4	**
3.78	6.0	—
3.92	—	1.7
4.93	1.6	*
6.03	2.5	**
10.23	**	10.7
10.65	*	7.3
13.03	12.6	—
13.31	—	11.4
16.69	**	54.7
29.43	2.2	3.4

* Peak with corresponding RT was absent.

** Peak with close RT was present as a minor (<1%) component.

Table II-6. GC Data for Ether Extracts of Lyophilized RAAP-NG-S

Retention time	Peak area for untreated sample	Peak area for neutralized sample
min	% of total	% of total
1.01	24.3	*
2.18	1.3	**
3.03	*	3.0
3.19	*	11.4
3.63	32.7	—
3.81	—	51.6
3.88	7.0	—
3.97	—	5.7
4.43	1.0	*
5.05	2.1	—
5.08	—	2.4
6.15	3.2	—
6.16	—	2.0
7.17	*	1.1
8.99	**	1.1
9.39	*	1.1
16.71	*	1.1
24.94	*	1.4
25.31	1.2	—
25.44	—	2.4
29.63	2.8	—
29.84	—	5.3
32.19	13.1	*

* Peak with close RT was present as a minor (<1%) component.

** Peak with corresponding RT was absent.

Table II-7. pH of NG Wastewaters Before and After Photolysis

Conditions	RAAP-NG-W	RAAP-NG-S
Unphotolyzed	8.97	10.24
With filter	8.74	10.12
Without filter	8.33	10.10

Table II-8. GC Data for Extracts of RAAP-NG-W After Photolysis
With and Without Pyrex Filter

Retention time	Sample		
	Unphotolyzed	Photolyzed	
		With filter	Without filter
min			
0.98	X	—	—
1.00	—	X	X
1.41	X	—	—
1.45	—	X	—
1.67	X	—	—
3.52	X	—	—
3.78	X	—	—
3.81	—	—	X
3.95	—	X	—
4.93	X	—	—
5.06	—	X	X
6.03	X	—	—
6.07	—	—	X
6.09	—	X	—
8.93	—	X	—
8.94	—	—	X
9.31	—	X	—
9.32	—	—	X
13.03	X	—	(*)
13.41	—	X	(*)
16.59	—	X	—
16.62	—	—	X
16.83	—	X	—
24.77	—	X	—
24.81	—	—	X
25.27	—	X	—
25.30	—	—	X
29.43	X	—	—
29.59	—	X	—
29.63	—	—	X

* Possible 2-MNG. These peaks tail significantly, reducing the precisions of the RTs.

Table II-9. GC Data for Extracts of RAAP-NG-S After Photolysis
With and Without Pyrex Filter

Retention time	Sample		
	Unphotolyzed	Photolyzed	
		With filter	Without filter
min			
1.01	X	X	X
1.46	—	X	—
1.72	—	X	—
1.85	—	X	—
2.18	X	X	—
3.61	—	X	—
3.63	X	—	—
3.64	—	—	X
3.87	—	X	—
3.88	X	—	—
4.41	—	X	—
4.43	—	—	—
5.03	—	X	—
5.05	—	—	—
6.13	—	X	—
6.15	—	—	—
8.70	—	X	—
16.62	—	X	—
21.89	—	—	X
22.83	—	—	X
24.75	—	X	—
24.84	—	—	X
25.31	—	—	—
25.33	—	—	X
27.28	—	—	X
29.52	—	X	—
29.63	—	—	—
29.68	—	—	X
32.19	—	—	—

When the plate was sprayed with DNPH, irradiated by ultraviolet light, then sprayed with DPA and again irradiated, the $R_f = 0.64$ spot had a dark rose color, and a new spot, also rose colored, appeared at $R_f = 0.41$. No other visualization technique would raise the latter spot.

IV. DISCUSSION.

Initial efforts to quantify the nitrate level in NG wastewater involved the use of a colorimetric technique. In this procedure, phenoldisulfonic acid (PDSA) is nitrated in anhydrous sulfuric acid to yield a product that is yellow in alkaline solution. The absorbance at 4100 Å is proportional to $[\text{NO}_3^-]$. In practice, this procedure proved to have a number of difficulties among which were (a) charring of organic compounds in the sample by the sulfuric acid; (b) time required for analysis, since each sample had to be measured and dried; (c) lack of stability of the PDSA reagent. The specific ion electrode has proven to be the faster and more reliable method.

The carbon and nitrate analyses demonstrate the basic character of these wastewaters. As expected, RAAP-NG-W is high in carbonate and inorganic nitrate, but quite unexpected is the higher carbonate level in RAAP-NG-S. Apparently, considerable sodium carbonate is carried over to the storehouse with the finished TNG. Since the nitric acid has been washed out by this time, the level of carbonate is essentially a function of the amount carried over and the rate at which the storehouse water is replaced. The high pH and high carbonate level have had another effect on these waters. By comparing the concentrations of organic carbon and organic nitrate, it can be seen that there has been extensive hydrolysis of the nitric ester functions, about 90% in RAAP-NG-W. In RAAP-NG-S, the only source of nitrate should be the TNG over which the water sits. The identical values obtained for organic carbon and inorganic nitrate indicate complete hydrolysis of TNG. This is substantiated by the small value for organic nitrate.

The high salt content of the RAAP-NG wastewaters permits lyophilization without risk of explosion from isolated TNG and DNGs. The salt acts as a diluent that stabilizes the TNG much as β -lactose does in the pharmaceutical preparation.

Preliminary GC investigations were made on liquid/liquid extracts of the wastewaters using chloroform, benzene, and other solvents. It was immediately observed that these contained a number of low-boiling-point compounds that eluted before or beneath the solvent peak. Diethyl ether was finally selected since it has a low boiling point and would dissolve all of the standard compounds. The efficiency of extraction based on percent of organic carbon removed may be misleading. The carbon and nitrate analyses showed that considerable hydrolysis had taken place in these wastewaters. If the primary end product of TNG hydrolysis is a very polar compound, such as glycerol, it would not be extracted by ether.

The GC analyses of the ether extracts of RAAP-NG-W and RAAP-NG-S make it clear that more is happening in these waters than simple hydrolysis of glyceryl nitrates. Each wastewater has an assortment of volatile organics, many of which may be charged, accounting for the dramatic changes in the chromatograms after neutralization. Also significant is the lack of strong peaks corresponding to the glyceryl nitrate isomers. Based on the carbon and nitrate analyses, none would be expected in RAAP-NG-S and none was observed. In the early chromatograms of the liquid/liquid extracts of RAAP-NG-W, peaks corresponding in RT to all

four standards were observed. After an elapsed time of about 2 months, the ether extracts of lyophilized wastewater were run and these peaks were absent. A repetition of the liquid/liquid extraction was done to determine whether the sample preparation method was the cause of the difference. Again, the NGs were absent and the chromatogram was quite similar to that obtained from the ether extract of the lyophilized samples. Apparently, the 2 months were sufficient for the hydrolysis of the NG isomers.

The complexity of these wastewaters is further compounded by photolytic activity. Both show a slight decrease in pH and lessening of yellow color upon irradiation through a Pyrex filter. Pyrex has a cutoff at approximately 300 nm and provides a good simulation of natural (sunlight) irradiation. Even with this essentially visible light irradiation, there are marked changes in the UV-Vis spectra and gas chromatograms.

Aside from confirming the presence of TNG, DNT, and MNG in RAAP-NG-W, the TLC data show the presence of two compounds that are not nitric esters. One seems to be clearly a carbonyl compound based on its response to DNPH spray. The other requires a more complex visualization procedure and speculation on structure will have to await additional data.

V. CONCLUSIONS.

These studies on the RAAP nitroglycerine wastewaters provide future workers in this area not only with baseline data but also with methods and precautions that will expedite their work. Methods have been described for determination of organic and inorganic carbon and nitrate.

The lyophilization, extraction, and gas chromatographic separation have shown that these wastewaters are a complex mixture of organic compounds in which the nitrated glycerines are but a small part, if present at all. This cannot but have a significant impact on the direction of toxicological studies associated with these wastes.

It has been shown that the GC fingerprints obtained from ether extracts of the wastewaters are a function of time (the duration from sampling to analysis), pH, and exposure to light. In any subsequent work with these waters, these variables must be carefully controlled to avoid obtaining misleading data.

The presence of a non-nitrated carbonyl compound in the wash-water waste stream had been demonstrated by TLC.

APPENDIX (PART II)

FIGURES

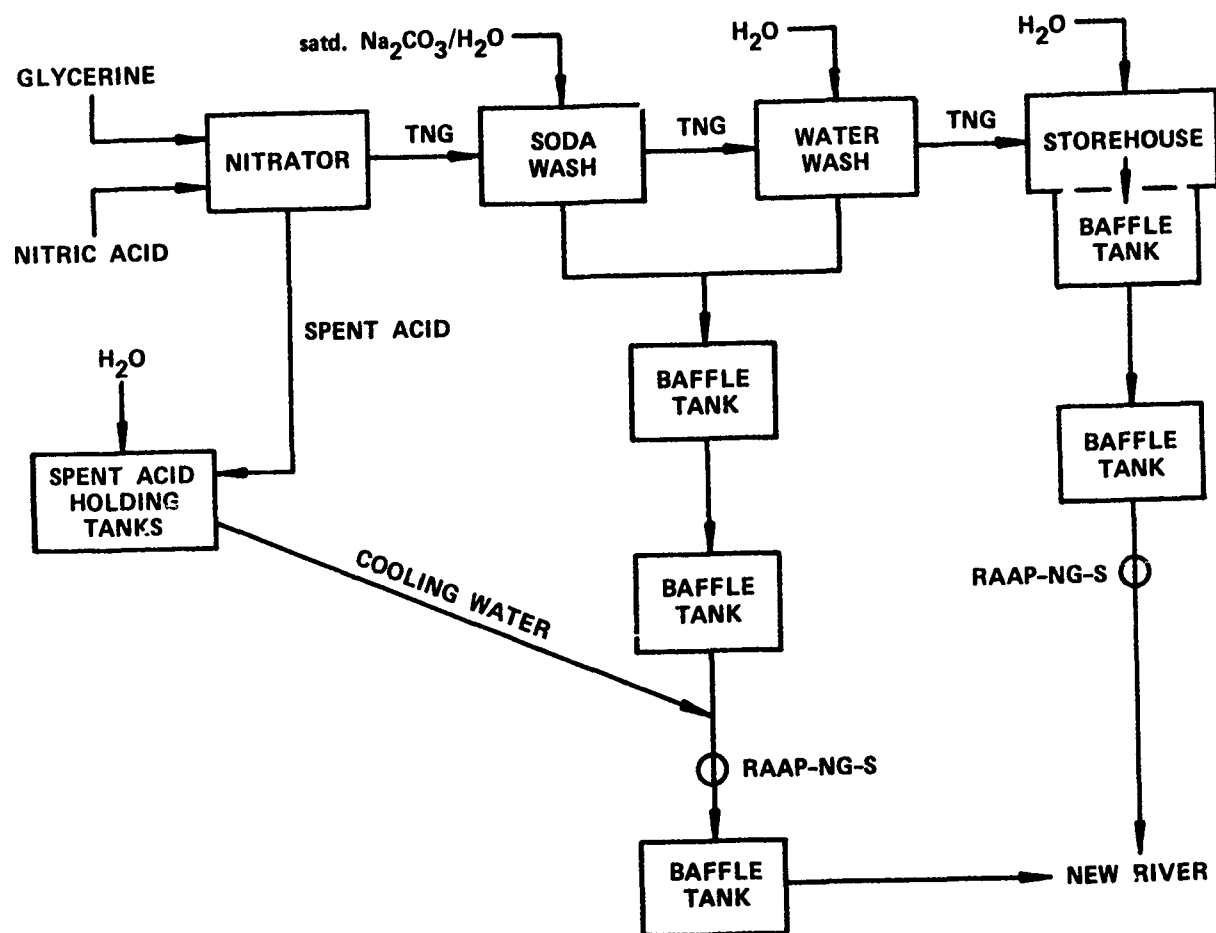


Figure II-A-1. Schematic of RAAP Nitroglycerine Production Facility Showing Waste Streams and Sampling Points

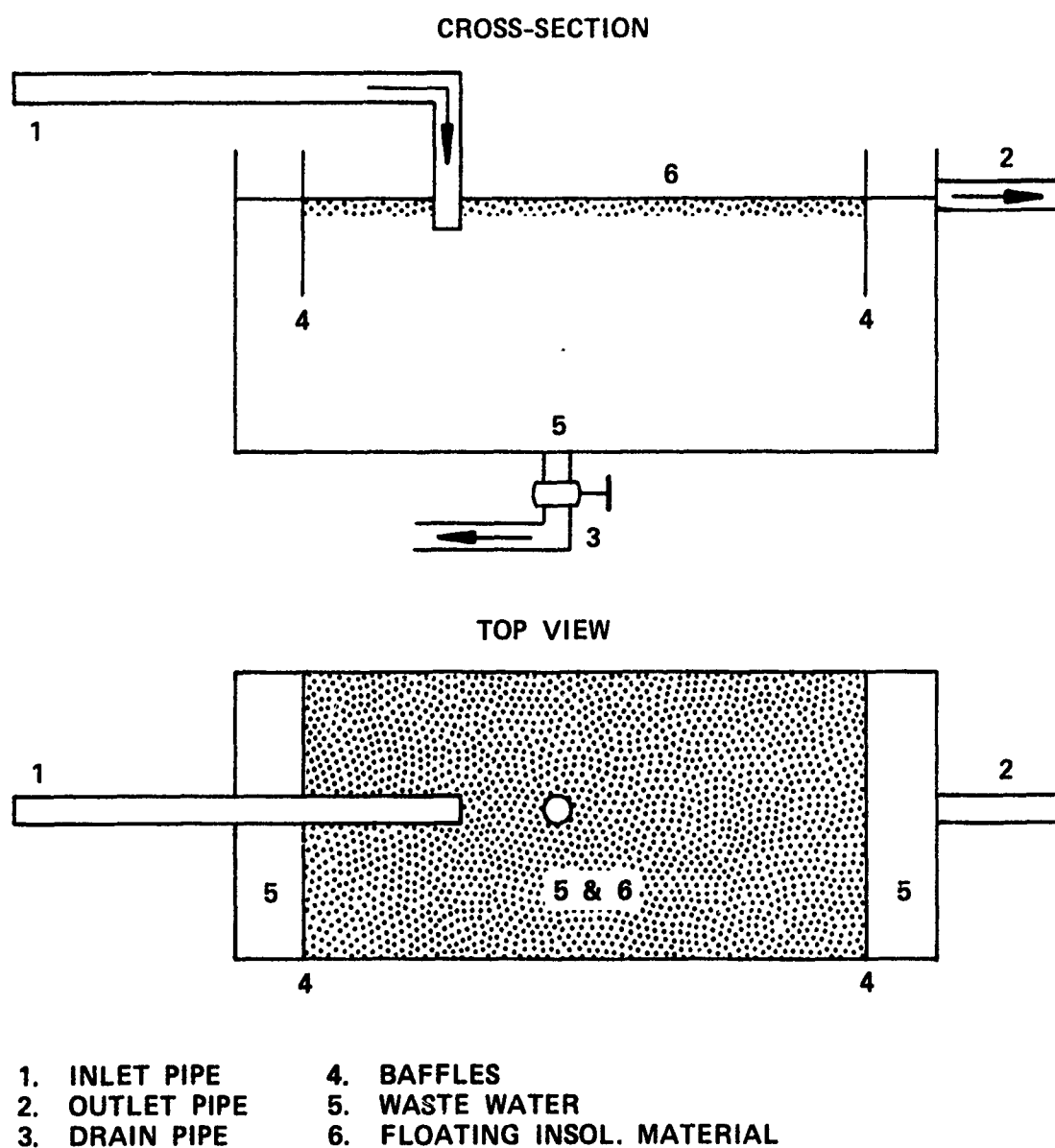


Figure II-A-2. Diagram of Baffle Tanks Used in NG Wastewater Streams at RAAP

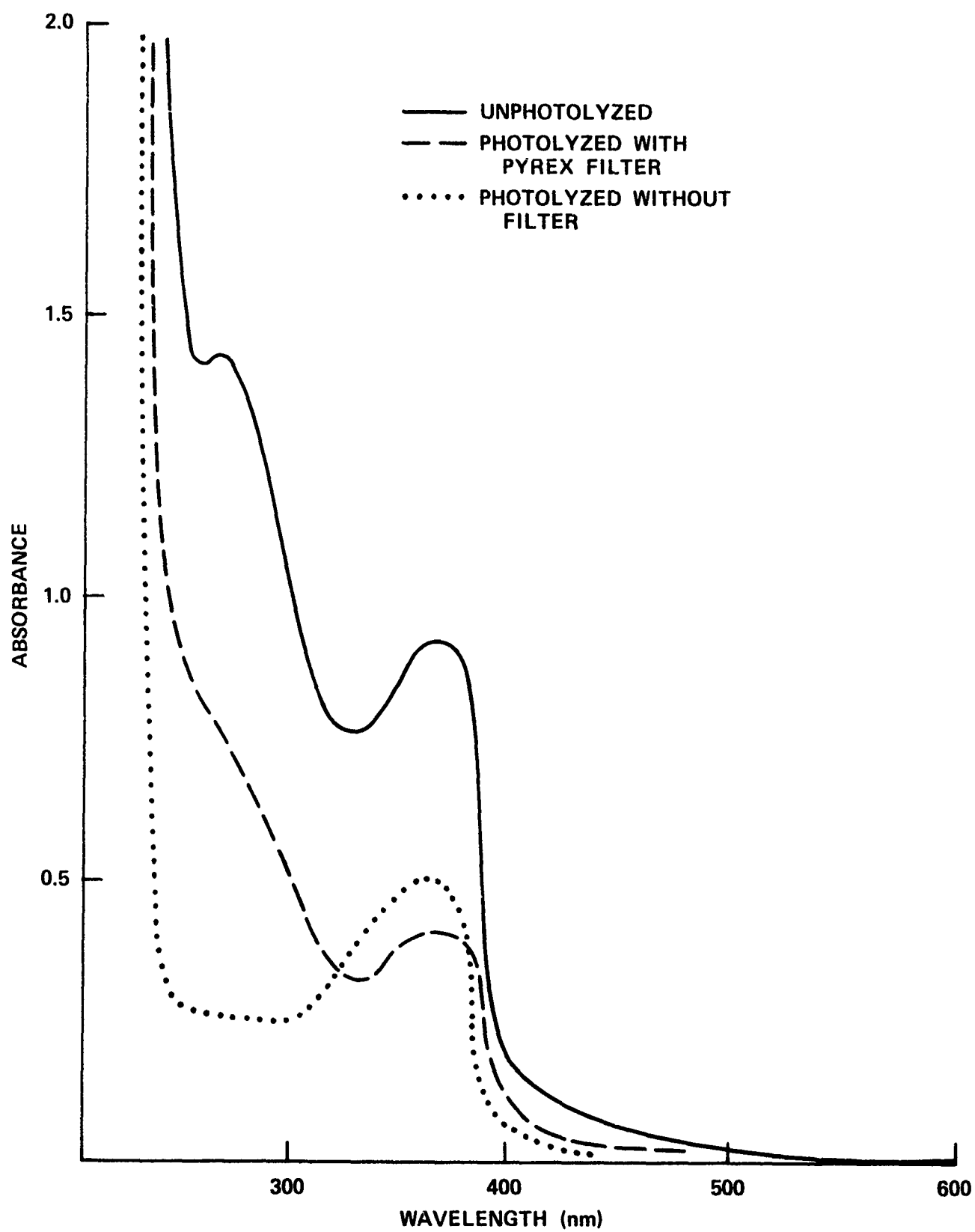


Figure II-A-3. UV-Vis Spectra of RAAP-NG-S After Varying Degrees of Photolysis

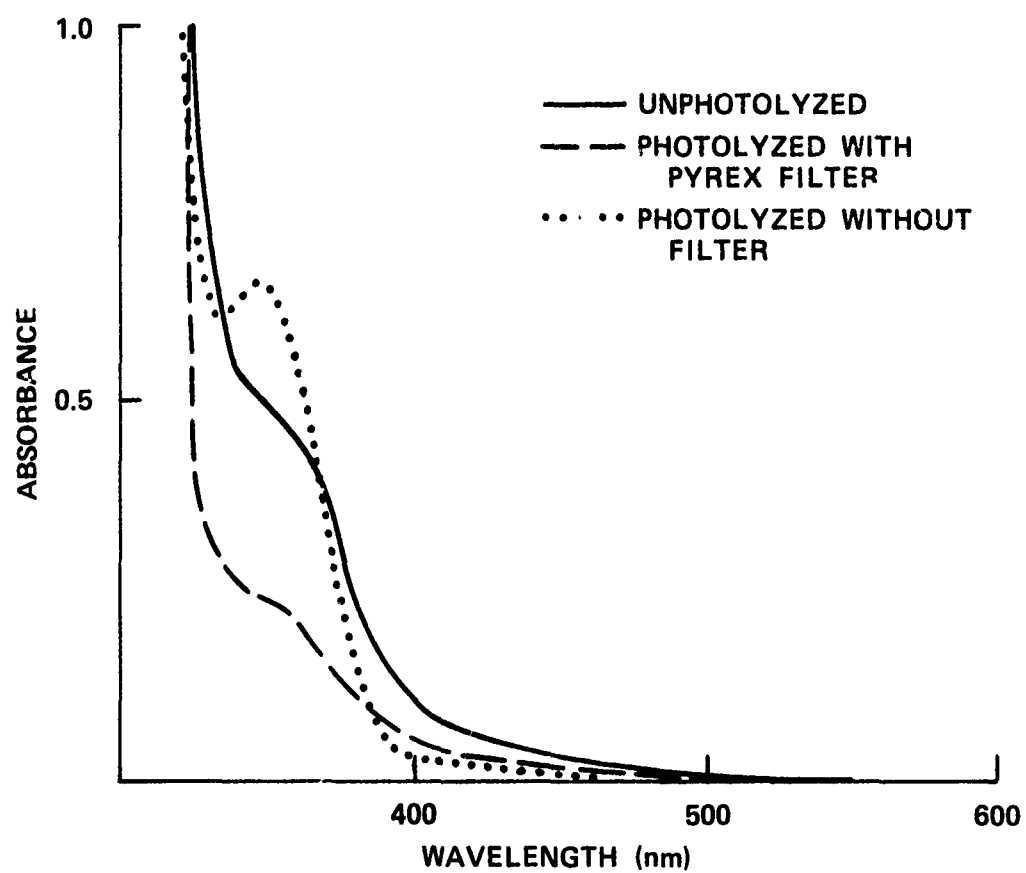


Figure II-A-4. UV-Vis Spectra of RAAP-NG-W After Varying Degrees of Photolysis

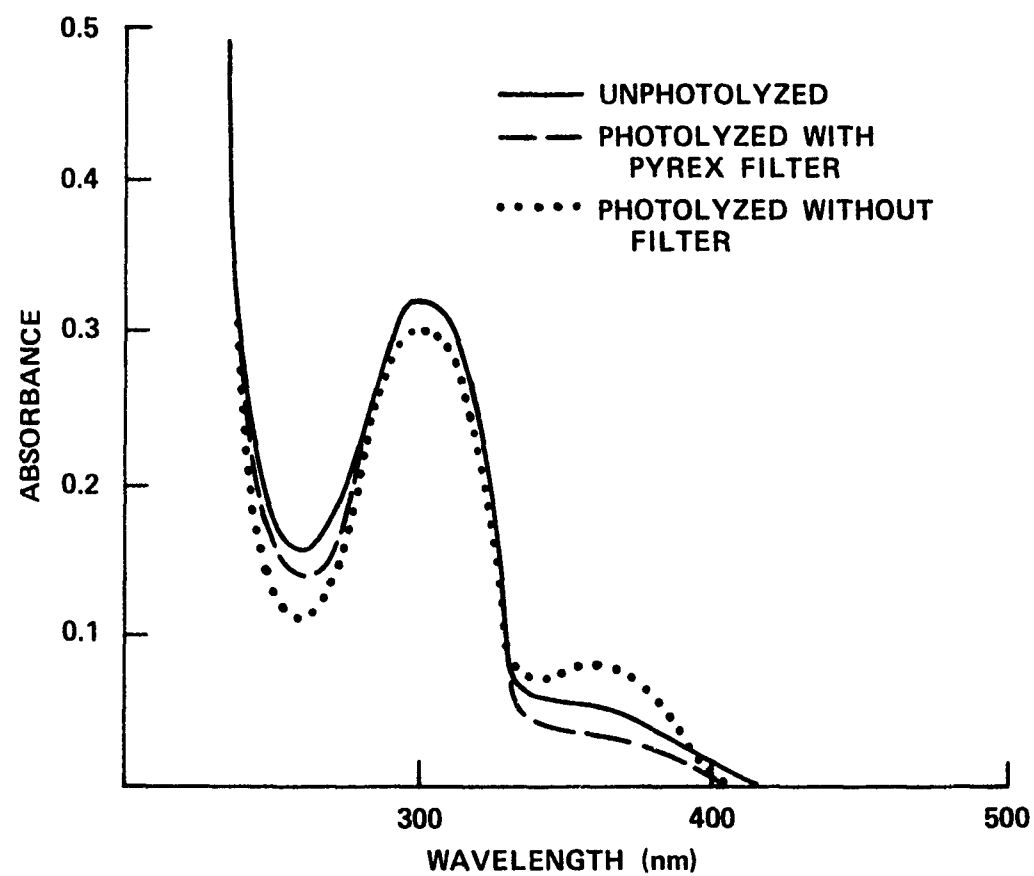


Figure II-A-5. UV-Vis Spectra of Diluted (1:10) RAAP-NG-W After Varying Degrees of Photolysis

ENVIRONMENTAL QUALITY STANDARDS RESEARCH ON WASTEWATERS OF
ARMY AMMUNITION PLANTS

PART III. CHARACTERIZATION OF NITROCELLULOSE WASTEWATERS

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PART III. CHARACTERIZATION OF NITROCELLULOSE WASTEWATERS

I. INTRODUCTION.

The immediate objective of this work was to generate information on wastewaters from nitrocellulose (NC) production that would permit the selection of typical organic nitrocellulose waste components for toxicological studies, ensure the proper description of toxicological samples, and guarantee the constancy of such samples during the course of extended toxicological investigations. Specifically, it was hoped to describe the particle-size distribution of nitrocellulose fines in terms of both number average and weight average, with the assumption that such particles would not vary significantly in elemental composition. It was also at first assumed that the solubility of nitrocellulose would be sufficiently low that its solubility in water could be ignored and that no significant amount of other organic substances would be present. Continued study of the systems has revealed that the distinction between aqueous insoluble and soluble materials cannot be so clearly defined.

II. BACKGROUND.

Nitrocellulose manufacture by Army ammunition plants is essentially as shown schematically in figure III which outlines the Radford Army Ammunition Plant (RAAP) process. In the RAAP process, dry cotton linters of pulp are mixed with a hot mixture of nitric and sulfuric acids. The acid is drawn off the reactor and recycles; the NC is poached, i.e., treated with several charges of boiling water. The NC goes through several steps of washing, blending, and screening. These operations require from 16 to 22 gallons of water per pound of NC. This water carries the waste material through settling pits into a settling lagoon, and the water eventually enters the river.

The final engineering report on the production engineering project PE-221¹ prepared by Hercules, Inc., on the continuous separation of NC and paste fines from plant effluent stated:

"A study was made of the present separation system to determine the efficiencies, the deficiencies, and the extent of the improvements required to meet the Ammunition Procurement and Supply Agency (APSA) proposed standard of 25 ppm suspended solids."

The report presented an evaluation of several methods for removing suspended NC from poacher pit water. Centrifugation was proposed for separating NC fines to less than the 25 ppm proposed by the APSA. The report on PE-221 contained a review of liquid-solid separation systems and also a discussion of the method presently used. This discussion about the current method of removal of fines is very pertinent to the situation at RAAP and also contains significant observations about removal of NC fines relevant to an observation in our studies of a sedimentation phenomenon in the poacher pit water induced by the addition of electrolytes.

The Hercules, Inc., Pollution Abatement Group had made a study of the NC purification waste process waters and had found considerable variation (80 to 900 ppm) in the amount of suspended solids in the wastewaters from the B-line boiling tub settling pits. The

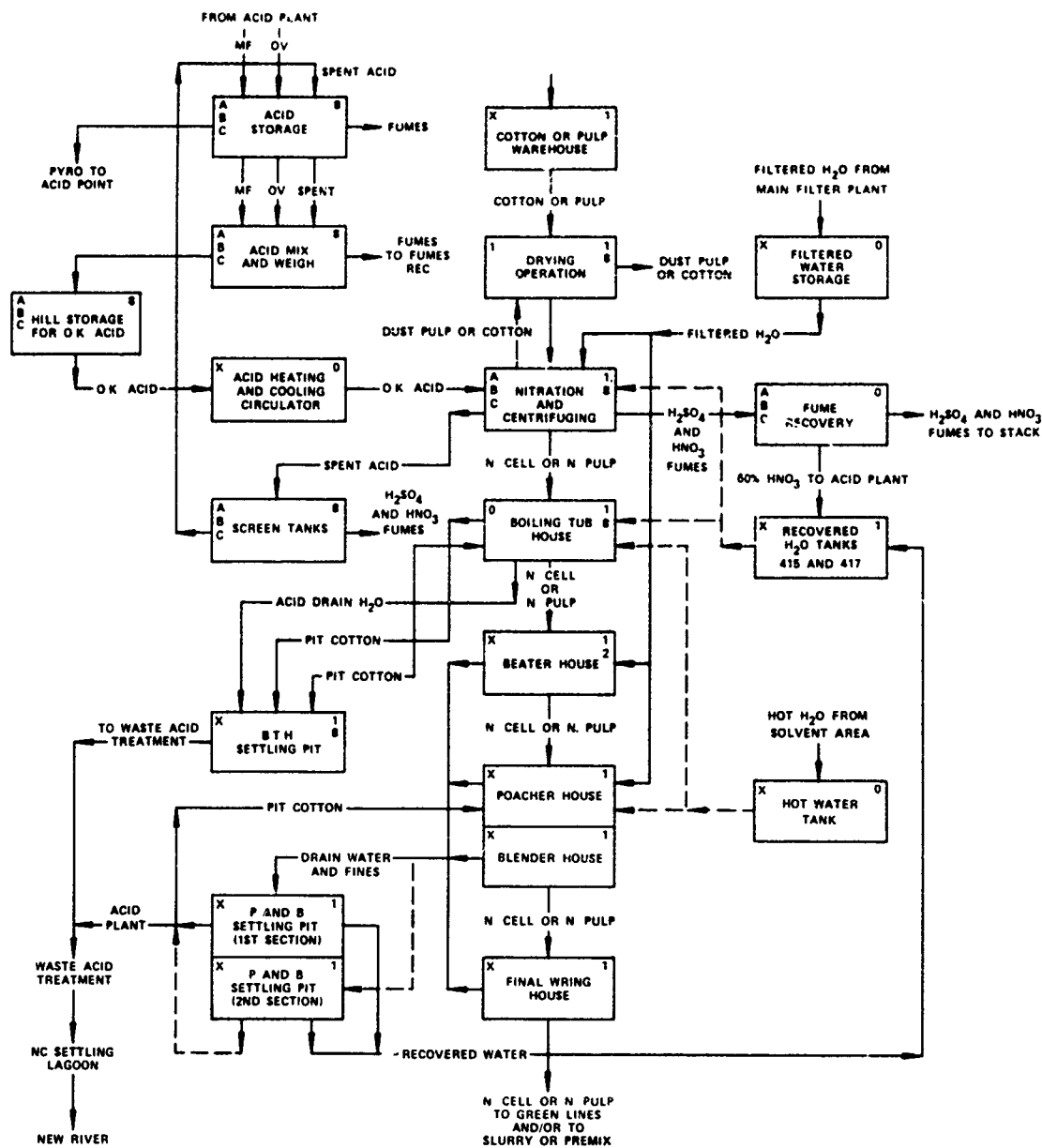


Figure III. Radford Army Ammunition Plant Process Schematic
(Nitrocellulose Manufacture)

suspended solids usually ran less than 200 ppm, but at times of high-volume production, and when large quantities of recovered water were being bypassed, suspended solids were considerably more than normal. This study estimated that more than 2 tons per day of suspended solids were overflowing the B-line boiling tub settling pits. More than 99% of the suspended solids were NC. The A-line boiling tub settling pit had an average discharge of only 8.2 ppm of suspended solids, but these pits did not have as much water volume and did not contain any recovered water.

Based on the studies conducted under PE-24,² the present system of removing NC was adopted. These studies showed that the amount of suspended solids in the wastewater from the NC purification area could be reduced by diverting the effluent from the poacher pits to the recovered water system and thence into the boiling tub settling pits. It was found that when the alkaline poacher pit waters were mixed with the acid waters from the boiling tub house, flocculation was increased and more NC fines settled out of the waste process water into the boiling tub settling pits under this system. The waste process waters from the beater, poacher, and wringer houses drain into the poacher pits where part of the suspended solids settle out. The waters, after passing through the poacher pits, overflow into a sump and, along with the blender tail water, are pumped to the recovered water tank. The waste process water from both A and B lines is pumped to the same recovered water tank, but the recovered water is only used in the B-line boiling tub house.

In the present system most of the recovered water (approximately 80%) bypasses the boiling tub house because of excess accumulations of solids in the recovered water storage tanks that could contaminate the in-process NC. This causes an increased flow of water through the boiling tub settling pits, which results in poor pit settling efficiencies, and the resultant high amount of suspended solids in the effluent. All observations and work on NC process water in the presently reported studies were made only on production lines A and B at RAAP. Another production line, C, was not examined nor were any other NC processes at other Army ammunition plants.

This description of the NC process water at RAAP and analysis of the ongoing work underscores the necessity, prior to further extensive characterization studies, for a complete evaluation of the NC processes at Army ammunition plants where potential sources of pollutants may originate to insure well planned sampling.

III. EXPERIMENTATION.

Studies to obtain information on the NC production wastewaters proceeded along two lines: (a) physical characterization according to ranges of size, shape, and physical appearance (such factors as color and state of aggregation of suspended particulates) and (b) chemical characterization to include a determination of whether water-soluble organic compounds result from the manufacture of NC. In connection with the physical studies, an appraisal was made of the following techniques for particle analysis: sieving, optical microscopy, electron microscopy, sensing-zone methods (e.g., Coulter counter method), sedimentation (incremental, cumulative, centrifugal, photosedimentation), elutriation, and light scattering.

Each of the techniques has its limitations. For example, sieving is a practical technique only for particles greater than $75\text{ }\mu\text{m}$; sensing-zone methods (such as that using the Coulter counter) run into difficulties when the shape of the particles under study departs greatly from spherical; light scattering methods are inadequate when a wide range of particle sizes and shapes is present.

A. Initial Samples of Poacher Pit Wastewater Supernatant from RAAP,
17-18 July 1973.

The sample at the site had a pH of 7.15, a temperature of 39°C to 40°C , cloudy tan to pale green color, and a turbidity of 170 Jackson turbidity units. It contained 23 ppm of inorganic nitrate nitrogen, 60 ppm of sulfate, and total dissolved solids of 470 ppm (2 hours after sampling). After transportation to Edgewood Arsenal, the concentration of solids in the supernatant collectable on a $0.45\text{-}\mu\text{m}$ millipore filter was 0.11 gm/liter; sonication was used to resuspend particulates that had precipitated during transit of the sample, thereby doubling the collectable solids concentration to 0.22 gm/liter. Some of the same poacher pit waste was subjected to pilot plant centrifugation at RAAP before shipment; it contained 0.06 gm/liter of solids in the supernatant. The three aqueous samples (supernatant, sonicate, centrifugate) contained, respectively, 0.0447, 0.0639, and 0.027 gm/liter of organic carbon determined by Beckman carbon analyzer). Particle size distribution determinations were attempted with an MSA sedimentation particle size analyzer; the results are not reported here because such determinations are only valid for approximately spherical particles.

Samples of the poacher pit water that had been filtered through a $0.45\text{-}\mu\text{m}$ millipore filter were extracted with methylene chloride, spotted with thin-layer chromatography (TLC) plates, and developed with various solvent combinations. The most successful experiments used benzene-acetone (1:9 by volume) developer and Quantum Industries Q1 TLC plates. Yellow spots were seen at $R_f = 0.95$ and $R_f = 0.40$. An additional spot ($R_f = 0.75$ to 0.80) was brought out by sulfuric acid charring or potassium permanganate bleaching, which are general visualizing methods for most organic compounds. This spot also appeared with *p*-anisidine-phthalic acid spray reagent, which is used in detecting sugars. All three spots gave an orange color with 1% DPA in sulfuric acid, a reagent for nitrates.

B. Microscopic Examination of Nitrocellulose Wastes.

A second sampling of RAAP wastewaters was made on 28 January 1974. Both supernatant and sediment samples were drawn from the poacher pits (PP) and from the nitrocellulose settling lagoon (LG) at RAAP. These were examined on 18-19 April 1974 by polarized light microscopy and scanning electron microscopy (SEM) at Walter C. McCrone Associates.

The McCrone report is presented in appendix A. Included in this report are SEM photomicrographs of evaporated residues of the NC wastewaters. The caption with each micrograph (figures III-A-1 to III-A-27) (appendix, part III) identifies the sample of NC wastewater and includes a brief description.

The report states -- "Judging by the retardation the nitrocellulose fibers exhibit under polarized light, they may have a varying degree of nitration." The PP sediment showed mostly white particles, but the LG sediment was brownish and appeared to contain iron oxides as well as possible cement debris. The supernatants contained few particles of any type. Electron microscopic examination required samples to be dried first on sample holders. When the water had evaporated, agglomerations of water-soluble needlelike (acicular) crystals could be observed in the LG samples; these were identified through energy dispersion X-ray analysis as calcium chloride. It is possible that the observed small granular residues were also left by the evaporating water. Neither the very small granules nor various rounded particles (from 0.1 to approximately 10 μm in size) visualized by SEM were necessarily nitrocellulose.

The SEM examination of the NC wastewaters has somewhat clarified the problem of characterizing the NC and has caused us to change or modify previous assumptions. Now the task is to progressively build up basic data on the NC wastewater systems and to modify procedures as data may suggest. SEM examinations as needed to complement the chemical characterization studies are desirable in understanding the NC wastewater systems.

C. Colorimetric Nitrite Method.

Nitrocellulose undergoes base-catalyzed (using concentrated sodium hydroxide) alpha-elimination, wherein nitrite ion and aldehyde or ketone are formed, along with hydrolysis to alcohol, OH, and nitrate ion; the formation of nitrite ion is the basis³ for an analytical method utilizing nitrite determination. It must be realized that the nitrite yield is unpredictably variable. A standard nitrite method⁴ involves diazotization with sulfanilic acid followed by coupling with 1-naphthylamine to form a highly colored compound.

An effort was made to apply a modification of this method to the determination of NC in wastewaters. Nitrite determinations followed the standard method,⁴ except for the substitution of *N*-(1-naphthyl)ethylenediamine dihydrochloride for naphthylamine hydrochloride. The colorimetric determination of NO_2^- was monitored on a Cary 14 recording spectrophotometer at 530 nm.

Conceptually, if all particulate NC could be removed from a wastewater sample by filtration, the presence of water-soluble RONO_2 components could be indicated by differential comparison of the amounts of nitrite in untreated (for inorganic nitrite) and base-treated NC process water. This approach was applied to poacher pit NC water that had been filtered through a 0.45- μm filter. The results suggested the presence of RONO_2 compounds in the filtrates. However, the later finding that the NC water contains particulates small enough to pass through such filters contraindicated this approach. Attempts to apply the nitrite method to unfiltered NC wastewaters gave random values in replicate tests, probably because of the heterogeneity of the samples.

D. Carbon Analysis of Nitrocellulose Wastewaters.

An Oceanography International Corp. total carbon system was used to examine various NC wastes collected in a third sampling of RAAP wastewaters, 28 May 1974. For consistent results (table III-1) it was necessary to use the ampoule method for samples with pH <4.5, whereas samples of pH >4.5 could be analyzed by the direct injection method.

Table III-1. Carbon Analysis of RAAP Nitrocellulose Wastewaters

Samples	pH	Inorganic carbon	Organic carbon	Total carbon
mg/l				
2A (NPR)	6.7	16	134	150
2B (NPR)	6.6	16	165	181
4A (NLR)	9.4	0	27	27
4B (NLR)	6.3	0	20	20
4E (NLR)	7.6	0	18	18
4D (NLR)	6.8	0	24	24
5AN (WAT)R	1.8	0	38	38
5BN (WAT)R	6.4	0	41	41
1AN (BTP)R	1.1	0	85	85
1BN (BTP)R	1.1	0	49	49
1B (BTP)R	1.3	0	75	75

BTP = Boiling tub settling pits.

NLR = Nitrocellulose lagoon, Radford.

NPR = Nitrocellulose poacher pit, Radford.

R = Radford.

WAT = Waste acid treatment.

Attempts were made to determine the dissolved carbon in the wastewater by filtering a composite sample of boiling tub settling pit (BTP) waste (not the samples mentioned in the table) through a series of filters, analyzing the filtrate for total carbon and comparing it with the original sample (unfiltered). Aliquots were filtered through millipore filters of successively smaller pore sizes. The results shown in table III-2 were obtained:

Table III-2. Carbon Analysis in Boiling Tub Pit Filtrate

Sample	Carbon concentration
	mg/l
Unfiltered	23.3
.8- μ m filtrate	23.5
.45- μ m filtrate	20.0
.1- μ m filtrate	18.75

These results are inconclusive. Perhaps a still finer filter would be required.

E. Other Studies.

Other work on NC wastewater from the RAAP poacher pits involved lyophilization, dialysis, liquid-solid extractions, adsorption, electrophoresis, and sedimentation studies. These several approaches were examined because the microscopic examination of NC wastewaters confirmed earlier suspicions of a complex microparticulate system. At this point we were seeking to establish a general characterization of the poacher pit wastewaters through several limited approaches. This section concludes with a brief account of some observations.

Suspended nitrocellulose particles in PP waters could be coagulated, and thereby settled out, both through the addition of electrolytes and through the removal of ionic solutes. Thus, either dialysis of a suspension or addition of such solutes as sodium chloride, calcium chloride, hydrochloric acid, and nitric acid brought about this effect (unexpectedly, sulfuric acid was less effective). This behavior is no doubt connected with the negative charge on nitrocellulose particles, which was demonstrated by observing with a light microscope the direction of migration of such particles in a low-intensity electric field. This type of behavior suggests the PP water is a sol consisting of colloidal particles. This sedimentation phenomenon now establishes a basis for characterization of at least the suspended solids in the PP water from which further studies can be extended.

Approximately 0.5 gram of cream-colored solid residue resulted from the lyophilization of 800 ml of PP water (surface sample). There was a noticeable difference in the colors of the lyophilized residues of dialyzed and nondialyzed PP water. Dialysis was performed in collodion dialysis tubing against distilled tap water at room temperature. Lyophilized, dialyzed PP water is much whiter than the nondialyzed material. This observation agrees with the observation that a yellow solution results when nondialyzed lyophilized PP wastewater residue is extracted with water in a Soxhlet extractor. Nonpolar organic solvents will not form a yellow solution in the Soxhlet extraction.

The yellow components from the Soxhlet extraction with water can be removed from solution by adsorption with animal charcoal (i.e., a colorless solution exists after passing through the charcoal). The adsorbate was not desorbed by common volatile organic solvents.

Attempts to observe movement by electrophoresis of components in the yellow water solution from the extraction were unsuccessful. However, movement was observed when untreated PP water was subjected to electrophoresis. Only enough work was done to establish a potentially fruitful and interesting approach.

Another observation of potential import is the formation of water-soluble yellow material in nitrocellulose suspensions, either on exposure to bright light or on heating near 100°C. This yellow color represented the edge of an absorption curve continually rising as it extended into the ultraviolet.

IV. DISCUSSION.

As is true of most chemical process industries, the concentration of impurities in the wastewater streams (in the absence of substantial equalization basins) fluctuates considerably. Upset conditions frequently cause the impurities (and here especially the settleable solids) to exceed prescribed norms. Thus, it is not enough to examine the supernatant water during periods of tranquillity. Samples should be taken when the water is roiled up, or as an alternative, samples of sediment should be examined. Sampling points should be chosen with care. As one goes downstream from the source (but still on the ammunition plant property) the particles of interest become diluted and mixed with relatively inert materials that interfere with identification. At the final outfall, the wastewater components are most difficult to characterize; the average particle size has dropped and dilution is the greatest. Yet it is precisely at the outfall that active pollutant particle characterization is most relevant to environmental hazard. Thus, research should progress from the concentrated pollutant of large average particle size upstream to the dilute pollutant of smaller average particle size downstream.

RAAP nitrocellulose process waters are complex for a variety of reasons. The cellulose used for nitration is either pure cotton linters or linters mixed with wood pulp cellulose. Some water is recycled, some not (figure III). It is especially noteworthy that excess recovered water from the recovered H₂O tanks finds its way to the boiling tub house settling pits. Periodically, surges of this carbonate-containing water are discharged into those settling pits with resultant foaming and carryover of large amounts of particulates.

Nitrocellulose itself is far from homogeneous. The degree of nitration can vary from sample to sample and quite possibly with particle size. Work at Midwest Research Institute (reported at the Symposium on Munitions Standards Research, Fort Detrick, Frederick, Maryland, November 1975) adds the following information on characterization of RAAP nitrocellulose wastes.

The sample was fractionated according to the ability of the particles to pass through various sieves and filters. References to particle size indicate the ability of particles to pass through these sieves and filters. The particle size ranges studied were as follows: $>88\text{ }\mu\text{m}$, <88 and $>44\text{ }\mu\text{m}$, <44 and $>5\text{ }\mu\text{m}$, <5 and $>0.8\text{ }\mu\text{m}$, <0.8 and $>0.2\text{ }\mu\text{m}$, $<0.2\text{ }\mu\text{m}$.

The percent nitration decreases abruptly as a function of particle size reaching a value of about 30% nitration for the <0.8 and $>0.2\text{-}\mu\text{m}$ sample. The samples in the particle size ranges of $>0.8\text{ }\mu\text{m}$ were all 80% to 95% nitrated. Differential thermal analysis suggests that the <0.8 and $>0.2\text{-}\mu\text{m}$ sample is low nitro-content nitrocellulose, but the $<0.2\text{-}\mu\text{m}$ sample contains little or no nitrocellulose. All particle sizes about $0.8\text{-}\mu\text{m}$ had about the same molecular weight, around $M_n = 60,000$. The $<0.8\text{-}\mu\text{m}$ samples had insufficient solubility for study by gel permeation chromatography or were of low molecular weight.

Along with fibers, there appeared rounded particles and granules in the electron micrographs of examined samples (but some of these may be water soluble substances rather than suspended particles). At this time, it is not certain that the rounded particles are even derived from cellulose. Sufficient material containing organic carbon penetrates even $0.1\text{-}\mu\text{m}$ filters, so that one cannot be sure just how soluble the nitrocellulose may be.

Continued investigation of nitrocellulose wastewater components requires restating the main questions in terms of what is now known. Among the problems that require answers, the following are most apparent:

1. Specification of sampling conditions and locations that would be most representative.
2. The identification or removal of inert particles or other components.
3. Specification of particle classifying techniques that would be most suitable for the range of greatest interest at the outfall (probably below $10\text{ }\mu\text{m}$).
4. Enumeration of the concentrations and identities of truly soluble organic compounds in the wastewater.

The chief value of the investigation to date has been the revelation of the kinds of effort and resources needed for further studies.

V. CONCLUSIONS.

Wet sieving and filtration are evidently adequate for separating nitrocellulose particles into ranges of particle size.* The objective is to use successively finer filters, down to 0.025 μm . Each filter should then hold a given size range of particles. The particles on a given filter should be washed with distilled water to remove dissolved solids.

The following are appropriate treatments for the particles classified above:

1. Drying (or lyophilization) and weighing
2. Total nitrogen analysis (or C, H, O, N analysis)
3. Total nitrate-ester nitrogen analysis, e.g., by titanous salt reduction and back titration
4. Nitrate-ester analysis by basic cleavage to form (in part) nitrite
5. Organic carbon analysis by difference between total organic carbon and inorganic carbon
6. Solution in an organic solvent and liquid-liquid, gel-permeation, or thin-layer chromatography
7. Microscopic analysis, including particle counting; use of scanning electron microscopy
8. Use of X-ray and electron probes for analysis of individual particles
9. Removal of slightly soluble (or almost insoluble) inorganic compounds by washing with chelating agents (e.g., oxalic acid for iron oxide)

Other possible studies of particle behavior include light scattering and coagulation with polyvalent cations.

Chemical study of the final filtrate (i.e., filtrate through a 0.025- μm filter) is desirable. If organic solutes are present, extraction of the organics with a solvent and TLC of the extracts should be feasible. Attempts might be made to subject the samples to gas chromatography/mass spectrometry, average molecular weight determination, or other chemical characterizations. Chemical and microscopic examinations should be coordinated.

The isolation of more than miniscule amounts of the smallest particles would be a tremendous undertaking. Nevertheless, these small amounts may be sufficient to determine mutagenicity.

* Midwest Research Institute, Contract No. DAMD-17-74-C-4072.

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APPENDIX (PART III)

MICROSCOPIC EXAMINATION OF NITROCELLULOSE WASTEWATER SAMPLES BY WALTER C. McCRONE ASSOCIATES, INC.

The McCrone report suggests the complex nature of the NC wastewater residues. There were four significant physical types of materials observed in the systems examined, excluding the crystalline rosettes, and therefore four potentially different chemical materials that should be considered. These types of materials are: (a) fibrous, (b) dispersed, (c) amorphous, and (d) spherical.

The four types of materials present in the wastewater residues are displayed in the SEM photomicrographs, figures III-A-1 through III-A-27, found at the end of this appendix. Figure III-A-1 displays the fibrous and dispersed materials from a PP sample. Some of the fibers are several hundred micrometers long and are presumably NC fibers. The layer of dispersed material in figure III-A-1 is present all over the residue sample spot. Figures III-A-2 and III-A-3 show the dispersed material under greater magnification and indicate that most particles are $<1\text{ }\mu\text{m}$. The presumably fibrous nature of NC prompts the question of whether this dispersed material having spherical particles of diameter $<1\text{ }\mu\text{m}$ is also NC.

Figure III-A-8 displays the amorphous material (right edge of residue spot) and spherical particles in a PP sample. Figure III-A-11 shows a great magnification of the amorphous material seen in figure III-A-8. Figure III-A-9 is a greater magnification of the spherical particles in figure III-A-8.

The micrographs of the residues from the settling lagoon (figures III-A-13 through III-A-27) display materials similar to those from the poacher pit with the addition of the crystalline rosettes (figures III-A-16, III-A-17, III-A-19, III-A-22 and III-A-24 through III-A-27). Figure III-A-18 represents an energy dispersion X-ray analysis spectrum of the crystalline rosette in figure III-A-17. The data indicate a high concentration of Ca and Cl in the crystal.

The following is the text of a letter report by John A. Brown, Research Associate, and Ian M. Stewart, Manager, Electron Optics Group, Walter C. McCrone Associates, Inc., Chicago, Illinois, dated 26 April 1974:

This letter reports the results of our examination of the four samples which you brought to us on 18 April and which were examined in your presence on 18-19 April. These were all samples of waste waters from nitrocellulose plants and were identified as follows (letters are our designations):

<u>McCrone SEM identification</u>	<u>Edgewood identification</u>
A	NC-H ₂ O-LG Sed RAAP
B	NC-H ₂ O-LG Sup RAAP
C	NC-H ₂ O-PP Sed RAAP
D	NC-H ₂ O-PP Sup RAAP

The suffixes "Sed" and "Sup" referred to sediment and supernatant liquid samples, respectively. As we received the samples, the PP Sed sample showed a large amount of white settled material; the LG Sed sample, on the other hand, was brownish in color. The samples were examined using a combination of polarized light microscopy and scanning electron microscopy.

The samples were first prepared for light microscopy. In the case of the sediment samples, these were shaken to resuspend the sediment, and a small drop of the liquid for each of the four samples was placed on a clean microscope slide which was then examined before the drop had dried. Both the sediment samples showed the presence of quite large fibers, those in the PP sediment being larger than those in the LG and also more numerous. These fibers ranged in size from a few micrometers in length right up to several hundreds of micrometers. In the LG sediment sample there were several particles which looked somewhat like cement debris and these were generally associated with some iron oxides which may have imparted the brownish color to the suspension. In the supernatant samples there were very few particles of any type; such as there were, were equant and extremely fine, and only an occasional fiber was observed. After allowing these samples to dry, they were examined in the dry state with the following results: the PP sediment, though it looked white by reflected light, had a brown film when viewed by transmission. This film looked something like a slime and it was not clear whether it was amorphous or an assemblage of fine crystalline particles. If the latter was the case, again it was not clear whether those particles had previously been in suspension or whether they had come out of solution. Some of the particles were therefore scraped from the edge of the dried drop (where the brown film appeared to congregate) and attempts were made to bring these particles into re-solution, but they did not dissolve.

In the LG sediment there was again a brown phase observed but unlike the PP sediment this phase did not form a ring around the dried drop but appeared to be disseminated in isolated patches throughout the preparation. At the edge of the drop were numerous crystalline "rosettes" which we believe had crystallized from the drying drop. Some isolated similar crystals were seen within the body of the sample. In the two supernatant samples the PP supernatant appeared similar to the previous PP supernatant with very finely disseminated particles throughout but with a brown ring around the periphery of the dried drop. The LG supernatant, however, showed the edge of the drop again ringed by recrystallized rosettes. One of these rosettes was adhering to the end of a fiber, but we believe that, rather than originating from the fiber, the fiber had nucleated the crystallization. Within the body of the dried drop there were some isolated crystals similar to those on the rosettes and a fiber within this area was decorated with crystals, again as though the fiber had nucleated the crystallization. One or two of these rosettes were separately picked from the edge of the dried drop of the LG supernatant and transferred to a clean, dry slide. A drop of water was then introduced to the slide and moved slowly toward the crystal. As the crystal became immersed in the water, it showed signs of going into solution and this was allowed to stand for some time. Although the crystal did not go completely into solution during the period of observation, probably due to saturation of the solution, it was obvious that this crystalline material was water soluble. The drop was then allowed to dry on the glass slide, and star- and rosette-shaped crystals again crystallized out at the periphery of the drying drop, confirming that the rosettes observed in the microscope preparations had resulted due to recrystallization of a dissolved phase. In another slide a halo denuded of small particles can be seen around the original crystal. Around the edge of this halo are numerous very small crystals developed, and these may be similar to the small, equant crystals previously noted and also observed on the scanning electron microscope. The denuded zone probably indicates a region of rapid diffusion of material to the central "nucleus" during recrystallization.

Scanning electron microscopic examination

Concurrently with the light microscopic examination, an SEM examination was made of the suspensions. For SEM examination the samples were prepared by placing one drop of the suspension as submitted on the glass cover slip mounted on an SEM specimen stub. These samples were then coated in a vacuum evaporator with both carbon and gold to prevent electrical charging while in the SEM. Descriptions of examples as observed in the SEM follow:

Sample NC-H₂O-PP Sed. This sample showed several fibers in a wide range of sizes as noted in the light microscopical examination. There were also some rounded particles in the 50- to 100 μ m size range, a fair number of rounded particles in the 5- to 10 μ m range and very many particles in the <0.5 μ m range. These fine particles go down to <0.1 μ m in size and the mass of these fine particles is apparently cemented together by an amorphous continuum which partly masks their definition (the brown slime observed by light microscopy?).

Sample NC-H₂O-LG SED. This sample is very similar to the previous sample but with less particulate material present. Additionally, however, the sample had a few large (100 to 200 μ m) well defined, acicular crystals, mostly at the edge of the dried drop, indicating crystallization from solution as the drop dried on the microscope sample mount.

Sample NC-H₂O-PP Sup. This sample showed some particles in the 0.5- μ m range, many particles in the 1- to 2- μ m range located near the dried drop edge and a significant amount of dried amorphous material at the extreme edge of the dried drop.

Sample NC-H₂O-LG Sup. This sample showed mostly fine, granular particles in the 0.1- to 0.3- μ m range and acicular particles, all partly covered with an amorphous coating which apparently came from solution. As in the case of the LG Sed sample there were also some large, acicular crystals located at the drop edge.

Since there was some amorphous material in these samples which had apparently come out of solution, there was some doubt as to whether some of the granular particulate materials had also been in solution. In an attempt to resolve this question portions of the two sediment samples were filtered on a 0.22- μ m size filter and washed with three changes of deionized water. The sediment was redispersed in deionized water and a drop of the suspension was dried on a SEM sample mount as with the original samples. One drop of the filtrate was also dried on a sample mount. Both were processed for examination as were the original samples and were given the following designations:

A-1. Sediment from filtering and washing LG sediment

A-2 Filtrate from filtering LG sediment

C-1. Sediment from filtering and washing PP sediment

C-2. Filtrate from filtering PP sediment

On examination in the SEM the following information was obtained:

A-1. The washed sediment from the LG sediment still showed a great mass of fine particulate material similar in distribution to that seen in the original sample. However, some amorphous material was also observed.

A-2. The filtrate from filtering and washing the LG sediment still showed some extremely fine particulate material now heavily buried in the amorphous component. There were also some large, acicular crystals as were observed in the original sample.

C-1. The sediment from filtering and washing the PP sediment showed a mass of fine particulate material similar to the original PP sediment. Again, some amorphous material was observed.

C-2. The filtrate from filtering and washing the PP sediment showed some very fine, granular material, again buried in an amorphous continuum. No large, acicular crystals were observed. The particles are not well defined and may be small isolated droplets of the amorphous material which form granules on drying.

Discussion and results.

From the examinations which we have carried out, it is clear that the effluent from nitrocellulose plants is not a simple system. In addition to the nitrocellulose fibers, we have observed a fine particulate material and an apparently amorphous phase. Judging by the retardation the nitrocellulose fibers exhibit under polarized light, they may have a varying degree of nitration. We believe at the present time that the fine particulate material is a dispersed phase although this has not been conclusively proven since the filtrates from the filtered and washed samples also show these fine particulate granules. The amorphous phase may or may not precipitate from solution and has the appearance on the light microscope of a brown slime and on the SEM as an amorphous continuum which frequently masks the morphology of the underlying particles. In the LG samples, we have an additional phase in the form of acicular crystals which precipitate from solution, often as rosette shaped aggregates.

As we discussed with you, it is probably better to try to more completely characterize the nature of the various components in the effluent before one is in the position to recommend means of

controlling this. Although the nitrocellulose fibers are the most noticeable feature of the samples, the brown material and the very fine particulate material require further characterization. At this stage we have not yet been able to confirm whether the very fine material was present as a dispersed phase or whether it came from solution, although we suspect it was present as a dispersed phase. Its presence, however, in the filtrate from the filtered and washed samples does raise some doubt, although the size of the particles observed are smaller than the nominal pore size of the filter used. As we discussed with you, there are further approaches which might be used to resolve this matter and we understand that you will be sending samples of the original suspensions after ultracentrifuging.

Also of significance are the acicular crystals observed only in the LG samples. Presumably these originate from the lagoon floor or walls, although it is also possible that they represent a phase leached from the walls of the PP basin. In either case it would be of interest to know whether this phase appears by normal aqueous solution or whether there is some component in the liquid phase of the effluent which promotes this solution attack.



Figure III-A-1. Scanning Electron Micrograph of Nitrocellulose Wastewater Residue from Poacher Pit at RAAP

The sample was prepared by evaporation of a drop of nitrocellulose wastewater. This indicates the variety of particle sizes and shapes. *1 mm on this micrograph equals 10 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-2. Scanning Electron Micrograph of Nitrocellulose Wastewater Residue from Poacher Pit at RAAP

This is the same sample as for figure III-A-1. This shows the finer material that is dispersed over the entire sample. *1 mm on this micrograph equals 1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

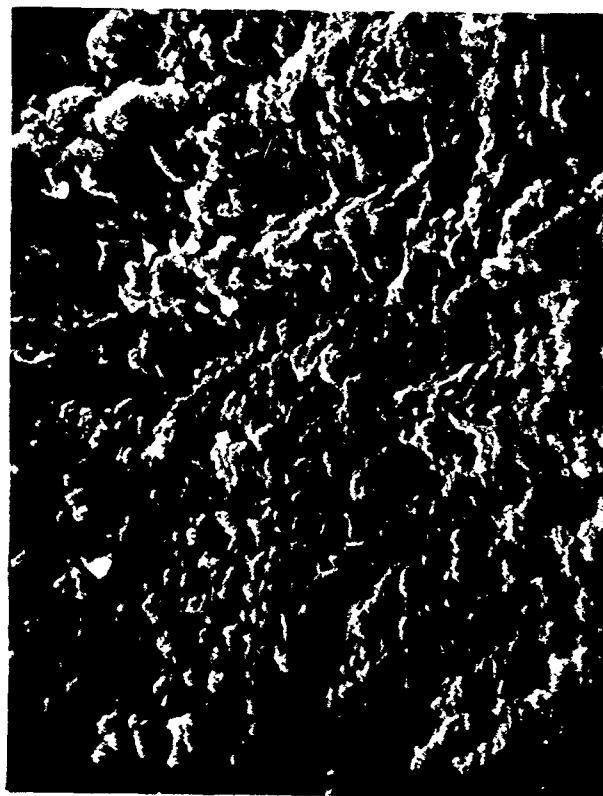


Figure III-A-3. Scanning Electron Micrograph of Nitrocellulose Wastewater Residue from Poacher Pit at RAAP

This is the same sample as for figure III-A-1. This greater magnification shows the fine dispersed material in more detail. *1 mm on this micrograph equals 0.1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-4. Scanning Electron Micrograph of Filtered (0.22- μ m-Pore-Size Filter) Nitrocellulose Wastewater Particles from Poacher Pit at RAAP Which Have Been Washed with H₂O

This suggests that the fine dispersed material is not readily soluble in H₂O. *1 mm on micrograph equals 0.1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

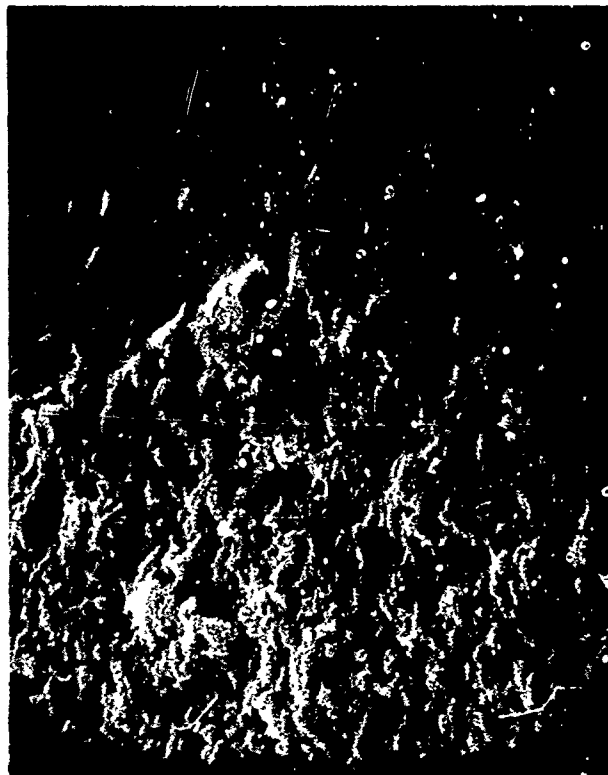


Figure III-A-5. Scanning Electron Micrograph of Filtered (0.22- μ m Pore-Size Filter) Nitrocellulose Wastewater Particles from Poacher Pit at RAAP, Which Have Been Washed with H_2O

This shows the edge of the sample residue spot which has a layer of amorphous material. 1 mm on this micrograph equals 0.2 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-6. Scanning Electron Micrograph of Evaporated Filtrate (from Sample C-1, Figure III-A-5)

1 mm on this micrograph equals 0.1 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

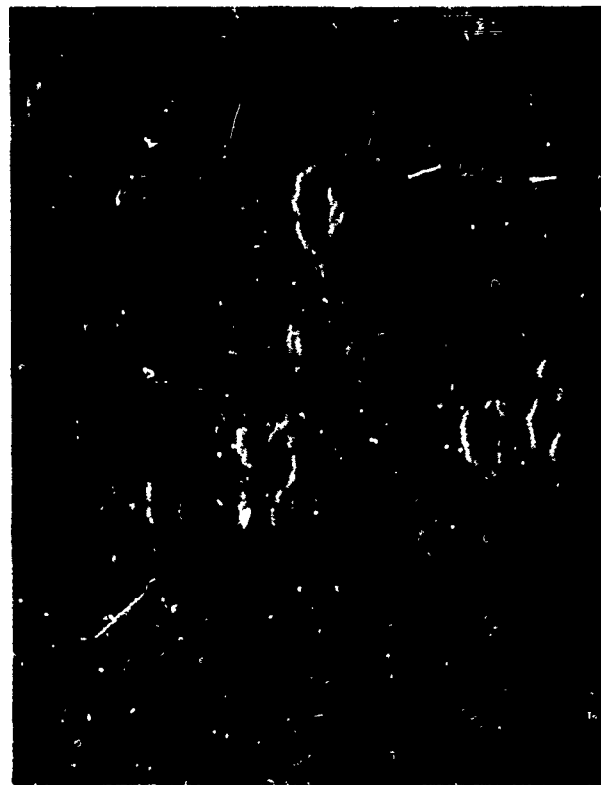


Figure III-A-7. Scanning Electron Micrograph of Evaporated Filtrate (from Sample C-1, Figure III-A-5)

1 mm on this micrograph equals 0.1 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

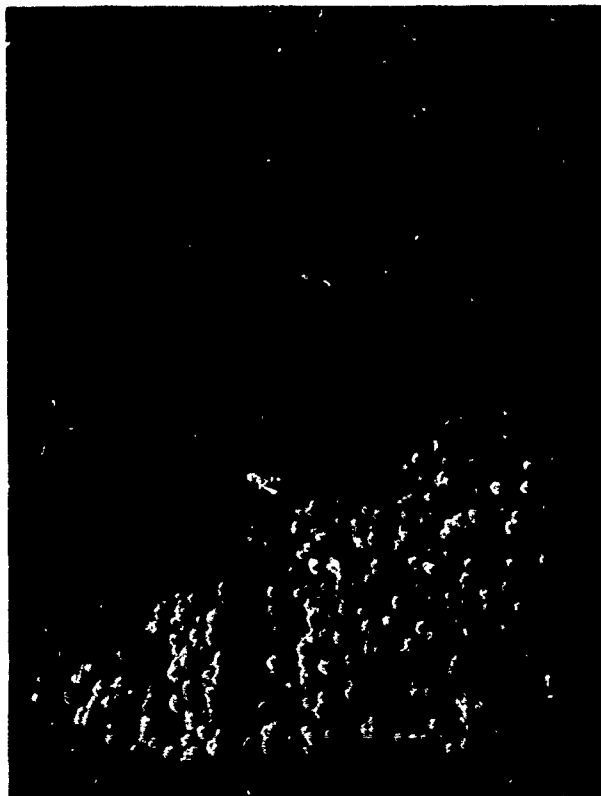


Figure III-A-8. Scanning Electron Micrograph of Particles in Supernatant of Poacher Pit Nitrocellulose Wastewater from RAAP

This is a site on edge of sample spot. 1 mm on this micrograph equals 1 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

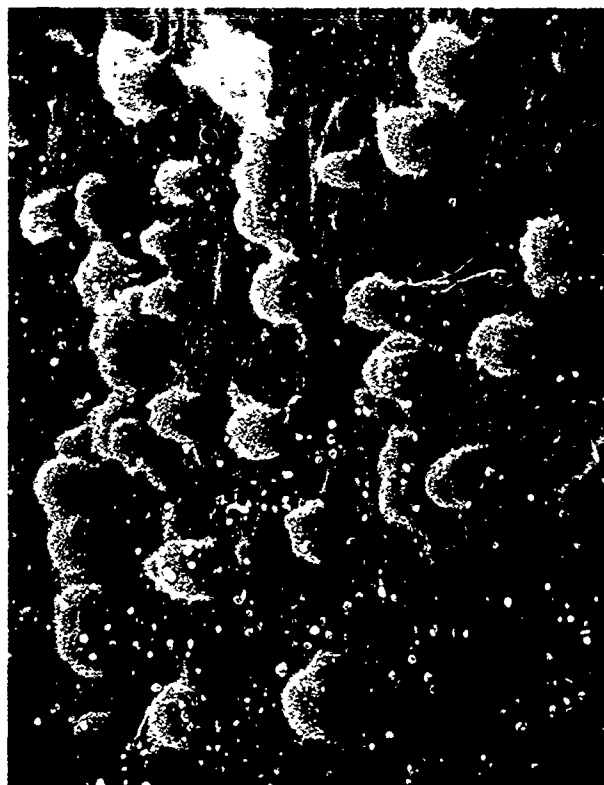


Figure III-A-9. Scanning Electron Micrograph of
Particles in Supernatant of Poacher Pit
Nitrocellulose Wastewater from RAAP

This is a magnification of the spherical particles in
figure III-A-8. *1 mm on this micrograph equals 0.2 μ m.* Micrograph
prepared by McCrone Associates, Chicago, IL. (April 1974)

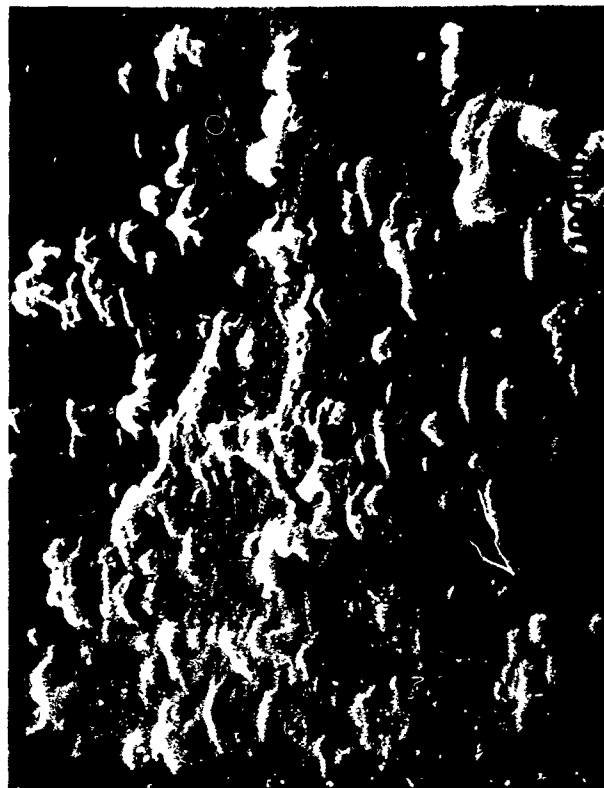


Figure III-A-10. Scanning Electron Micrograph of
Particles in Supernatant of Poacher Pit
Nitrocellulose Wastewater from RAAP

This is an internal site on sample spot. *1 mm on this micrograph equals 0.1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

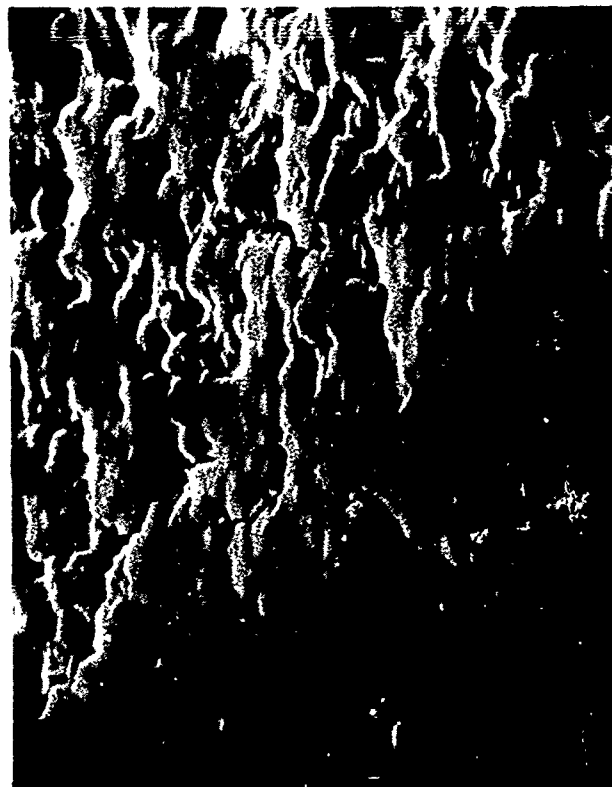


Figure III-A-11. Scanning Electron Micrograph of
Particles in Supernatant of Poacher Pit
Nitrocellulose Wastewater from RAAP

This is a magnification of a site on the extreme edge of sample spot showing the amorphous material. *1 mm on this micrograph equals 0.1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-12. Scanning Electron Micrograph of
Particles in Supernatant of Poacher Pit
Nitrocellulose Wastewater from RAAP

This is an internal site on sample spot. *1 mm on this micrograph equals 0.05 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

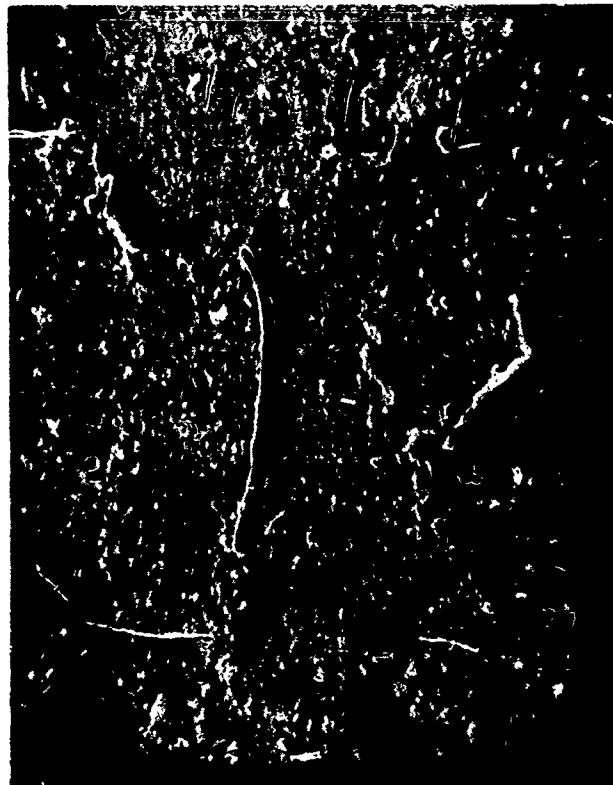


Figure III-A-13. Scanning Electron Micrograph of
Nitrocellulose Wastewater Residue from
Settling Lagoon at RAAP

The sample was prepared by evaporation of a drop of nitrocellulose wastewater. This indicates the variety of sizes and shapes of the particles. *1 mm on this micrograph equals 10 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

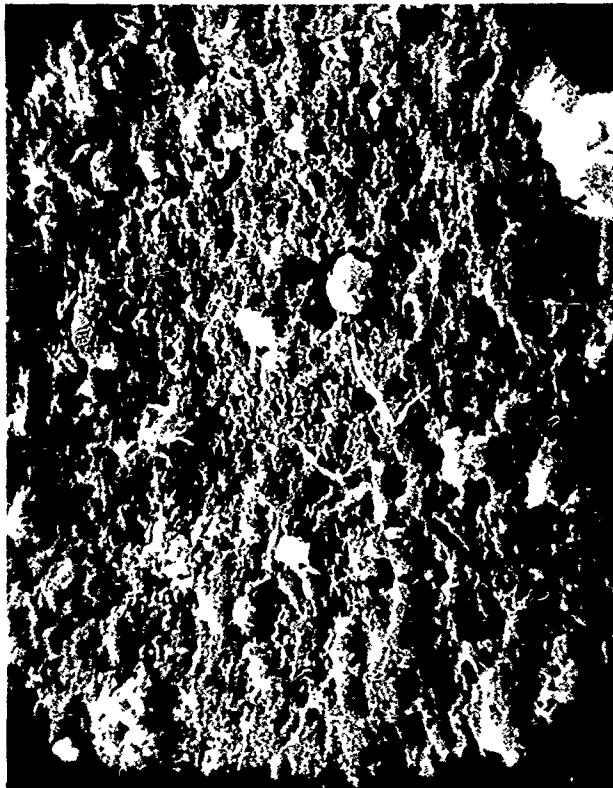


Figure III-A-14. Scanning Electron Micrograph of
Nitrocellulose Wastewater Residue from
Settling Lagoon at RAAP

This is the same sample as shown in figure III-A-12. *1 mm on this micrograph equals 1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

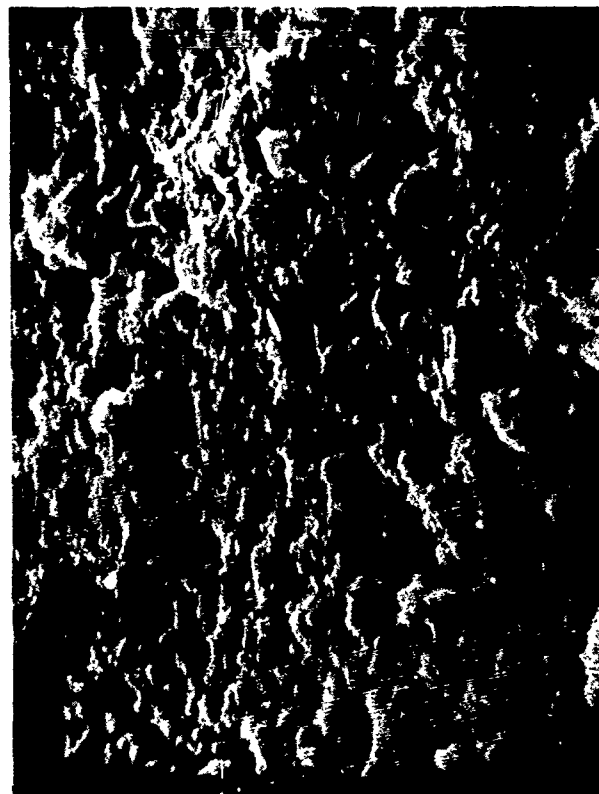


Figure III-A-15. Scanning Electron Micrograph of
Nitrocellulose Wastewater Residue from
Settling Lagoon at RAAP

This is the same sample as shown in figure III-A-12. 1 mm on this
micrograph equals 0.1 μ m. Micrograph prepared by McCrone
Associates, Chicago, IL. (April 1974)

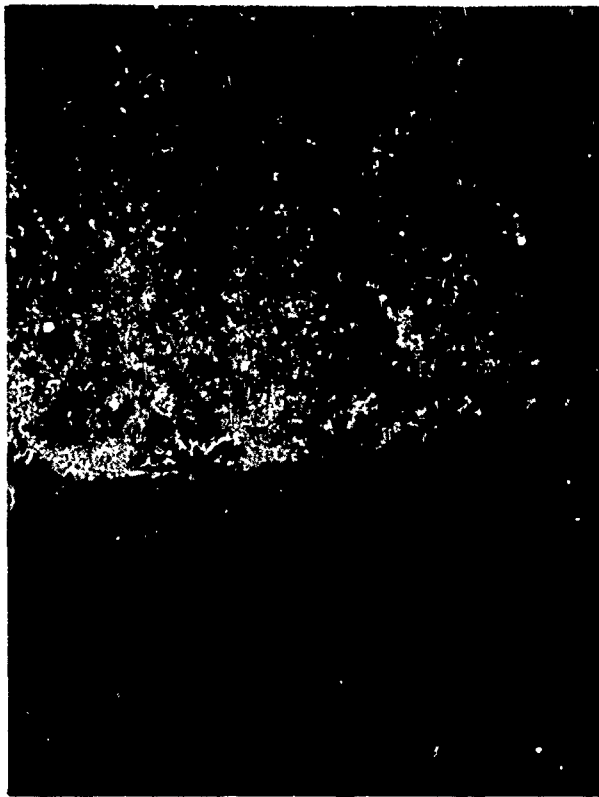


Figure III-A-16. Scanning Electron Micrograph of
Nitrocellulose Wastewater Residue from
Settling Lagoon at RAAP

This is the same sample as shown in figure III-A-12. This is the edge
of sample spot showing crystalline material at the very edge. 1 mm
on this *micrograph equals 20 μ m*. Micrograph prepared by McCrone
Associates, Chicago, IL. (April 1974).



Figure III-A-19. Scanning Electron Micrograph of
Nitrocellulose Wastewater Residue from
Settling Lagoon at RAAP

This is the same sample as shown in figure III-A-12. This shows the edge of the sample spot. *1 mm on this micrograph equals 1 μ m.* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

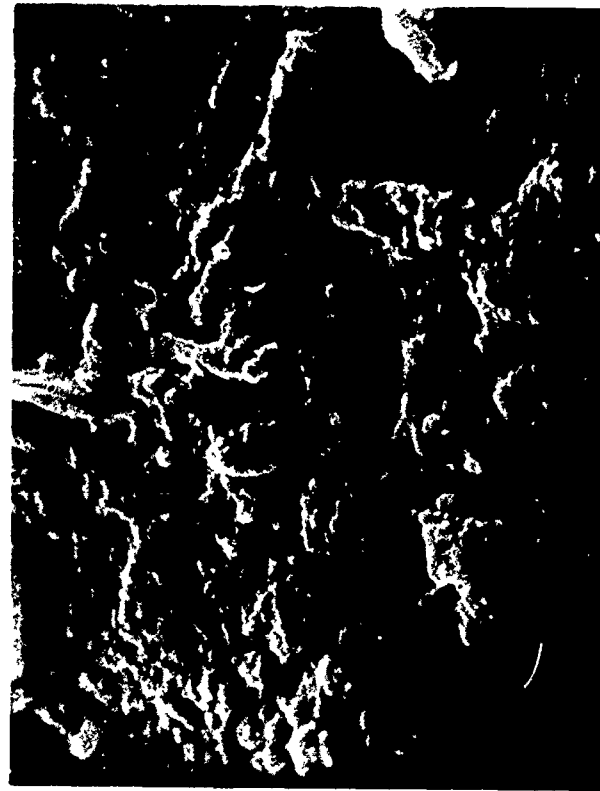


Figure III-A-20. Scanning Electron Micrograph of
Filtered (0.22- μ m-Pore-Size Filter)
Nitrocellulose Wastewater Particles from
the Settling Lagoon at RAAP, Which
Have Been Washed with H₂O

1 mm on this micrograph equals 0.1 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

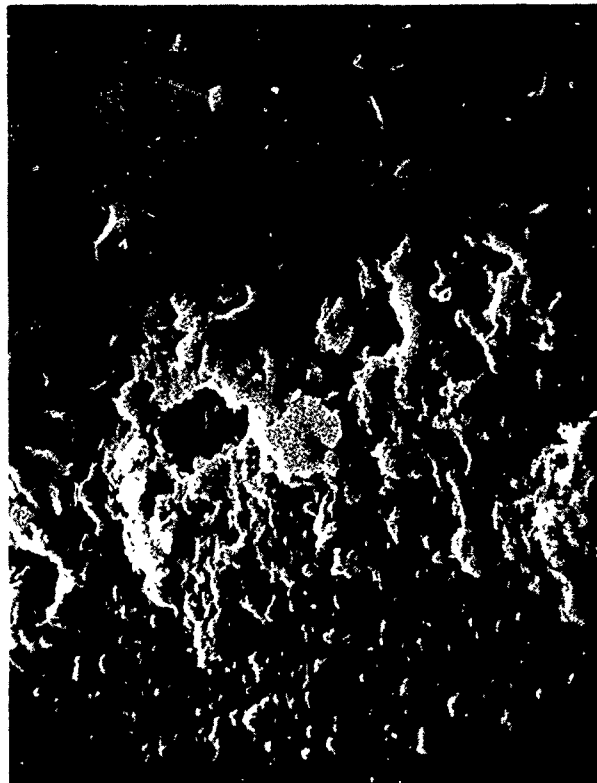


Figure III-A-21. Scanning Electron Micrograph of
Filtered (0.22- μ m-Pore-Size Filter)
Nitrocellulose Wastewater Particles from
the Settling Lagoon at RAAP, Which
Have Been Washed with H₂O

This is a site at the edge of the sample spot showing the amorphous material that appears somewhat smooth. 1 mm on this micrograph equals 0.2 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

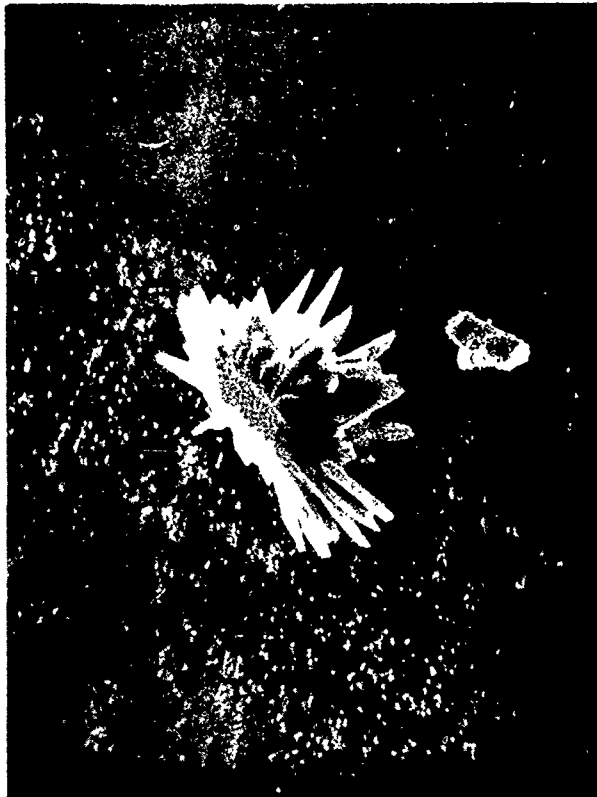


Figure III-A-22. Scanning Electron Micrograph of Evaporated
Filtrate (from Sample A-1, figure III-A-20)

This is a site at the edge of the sample spot. 1 mm on this micrograph equals 2 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-23. Scanning Electron Micrograph of Evaporated Filtrate (from Sample A-1, figure III-A-20)

This is an internal site of the sample spot. 1 mm on this micrograph equals 0.1 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-24. Scanning Electron Micrograph of Residue and Particles from Supernatant of Settling Lagoon Nitrocellulose Wastewater at P.A.A.P.

This is a site at the edge of the sample spot. 1 mm on this micrograph equals 20 μ m. Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-25. Scanning Electron Micrograph of
Residue and Particles from Supernatant of
Settling Lagoon Nitrocellulose
Wastewater at RAAP

Shows magnification of crystal at edge of sample spot. *1 mm on this micrograph equals 2 μm .* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)

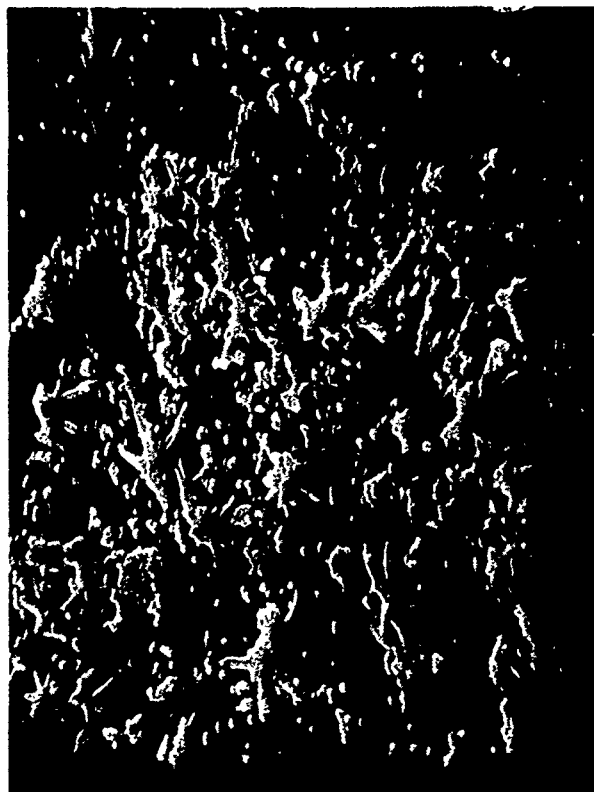


Figure III-A-26. Scanning Electron Micrograph of
Residue and Particles from Supernatant
of Settling Lagoon Nitrocellulose
Wastewater at RAAP

This is an internal site of the sample spot. *1 mm on this micrograph equals 1 μm .* Micrograph prepared by McCrone Associates, Chicago, IL. (April 1974)



Figure III-A-27. Scanning Electron Micrograph of
Residue and Particles from Supernatant
of Settling Lagoon Nitrocellulose
Wastewater at RAAP

This is an internal site of the sample spot. *1 mm on this
micrograph equals 1 μ m.* Micrograph prepared by
McCrone Associates, Chicago, IL. (April 1974)

GLOSSARY OF ACRONYMS AND ABBREVIATIONS

AAP	Army ammunition plant
APSA	Ammunition Procurement and Supply Agency
BAAP	Badger Army Ammunition Plant
BTP	boiling tub settling pit
CB	catch basin
DCIP	dichloroindophenol
DMSO	dimethyl sulfoxide
DNPH	dinitrophenylhydrazine
DNT	dinitrotoluene
DPA	diphenylamine
EDA	ethylenediamine
GC	gas chromatography
GC/MS	gas chromatography/mass spectroscopy
GLC	gas-liquid chromatography
GOCO	Government-owned, contractor-operated
HAAP	Holston Army Ammunition Plant
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high-pressure liquid chromatography
IR	infrared
JAAP	Joliet Army Ammunition Plant
LAAP	Louisiana Army Ammunition Plant
LAP	load, assemble, and pack
LC	liquid chromatography
LG	lagoon

MNG	mononitroglycerine
NC	nitrocellulose
NG	nitroglycerine (glyceryl trinitrate)
NLR	nitrocellulose lagoon, Radford AAP
NMR	nuclear magnetic resonance
NPR	nitrocellulose poacher pit, Radford AAP
PDSA	phenoldisulfonic acid
PF	post filter
PP	poacher pit
RAAP	Radford Army Ammunition Plant
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RT	retention time
Sed	sediment
SEM	scanning electron microscopy
SGO	Surgeon General's Office
Sup	supernatant
TBAS	tetrabutylammonium sulfate
TLC	thin-layer chromatography
TNB	trinitrobenzene
TNBA	trinitrobenzaldehyde
TNG	trinitroglycerine
TNT	trinitrotoluene
TOC	total organic carbon
UV-Vis	ultraviolet-visible
VAAP	Volunteer Army Ammunition Plant
WAT	waste acid treatment

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